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**Report**

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1st February 1993 - 31st March 1993

Principal Investigator: Dr Robin John Neat

**LITHIUM POLYMER BATTERIES FOR  
SPACE POWER APPLICATIONS**

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March 1993

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## Executive Summary

This report documents the results of the work performed by AEA Technology under contract number F61708-92-C0039 over the period 1<sup>st</sup> February 1993 to 31<sup>st</sup> March 1993 and represents deliverable item 004.

The US Air Force is undertaking a number of projects aimed at developing new and improved secondary battery systems for the provision of baseload power in satellites.

This project has the objectives of evaluating the Lithium Polymer Battery (LPB), developed by AEA Technology, against a GEO satellite duty cycle, and subsequently developing the battery system with a view to improving on its performance. A Mark I LPB cell has been defined as a lithium metal anode, lithium-ion conducting polymer electrolyte ( $\text{PEO}_{12}:\text{LiClO}_4$ ) and a composite cathode based on  $\text{V}_6\text{O}_{13}$ . The chosen operating temperature is 120°C. The space power duty cycle employed for the evaluation is a fixed discharge time of 72 minutes and a total charging time of 10 hours.

This report documents the results of experiments designed to evaluate the variables of depth of discharge (DoD), discharge current density and charging method on the performance of LPB cells with cathode capacities of 2.5 mA h cm<sup>-2</sup> and 1.15 mA h cm<sup>-2</sup>. For the Mark LPB cell with a 2.5 mA h cm<sup>-2</sup> capacity cathode the use of constant current charging result in a performance improvement over a mixed constant current and potentiostatic hold regime for DoDs of 20%, 40% and 60%. Cells cycling at 20% DoD with a constant current charge have performed 110 cycles (four percent energy loss over the first 100 cycles), and remain on test. Cells cycling at 40% DoD with a constant current charge have performed 70 cycles, and remain on test. The projected energy densities for optimised Mark I LPB cells (unpacked) cycling under these conditions are approximately 50 W h kg<sup>-1</sup> (20% DoD) and 100 W h kg<sup>-1</sup> (40% DoD).

Mark I LPB cells with cathode capacities of 1.15 mA h cm<sup>-2</sup> have been successfully cycled at C/1.5 rate (80% DoD). Further cycling data are required to determine whether this configuration of the Mark I LPB cell (i.e. high rate / lower energy density) exhibits any performance improvement.

A dramatic build-up in cell impedance has been identified with a performance limitation of the Mark I LPB. Three terminal a.c. impedance measurements indicate this is mainly cathode-related, and therefore may be associated with the cathode material  $\text{V}_6\text{O}_{13}$ .

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## **1. Objectives of Research and Statement of Work**

### **1.1 Introduction and Objectives**

The provision of baseload power for space vehicles remains a major technological challenge. The most common solution, used exclusively in satellites, is the combination of photo-voltaic cells and secondary batteries. The performance of current state-of-the-art secondary batteries is poor; they are bulky and heavy.

It is clear that an improvement in secondary battery technology would provide a significant payoff in terms of performance, survivability and affordability. Currently the majority of satellites fly with Ni-Cd batteries. These suffer from being both heavy and bulky (energy density 25-30 W h kg<sup>-1</sup> and 50-60 W h litre<sup>-1</sup>).

The US Air Force is undertaking a number of projects aimed at developing new and improved secondary batteries for satellite power applications. This report documents work carried out by AEA Technology under contract F61708-92-C0039 which has the object of evaluating the AEA-developed Lithium Polymer Battery against the GEO satellite duty cycle, and subsequently undertaking a development program to improve the battery's performance.

The Lithium Polymer Battery (LPB) is an all solid-state system which combines a lithium ion conducting polymer electrolyte with two lithium ion reversible electrodes. The polymer electrolyte also acts as a mechanical separator for the two electrodes. In most cases the anode is a metallic lithium foil. The cathode is typically a reversible intercalation compound such as V<sub>6</sub>O<sub>13</sub> or TiS<sub>2</sub> in the form of a composite backed by a metal foil current collector. LPB cells are fabricated by lamination of the three component layers; lithium foil, polymer electrolyte and composite cathode. The LPB concept has a number of advantages based on the all-solid-state construction; high energy density, high power density, good shelf life and excellent safety characteristics.

This project is the first phase of a three-phase program designed with the objective of translating the promise of the LPB technology into prototype battery units.

### **1.2 Statement of Work**

The statement of work (SOW) specifies the requirements for AEA Technology to evaluate the lithium polymer battery against the GEO satellite duty cycle, and subsequently undertaking a development program to improve the battery's performance. AEA Technology is performing three work packages in order to achieve the objectives of the program. These are illustrated in the work

breakdown structure in Figure 1.

Work package 1 will be performed from the program start for nine (9) months, although the electrical testing phase may be allowed to continue if results are promising. Work package 2 will run from month nine (9) to month twenty three (23) and is designed to follow on from work package 1. Work package 3 will be performed from month three (3) to month (21) and is designed to run concurrently with work packages 1 and 2.

#### **Work Package 1.**

AEA Technology will draw up a specification for the Mark I LPB which will be the most advanced version of the  $V_6O_{13}$ -based LPB at the start time of the contract. AEA Technology will use its facilities in the Lithium Battery Section of the Applied Electrochemistry Department to test the cycle performance of the Mark I LPB cell against the following variables: a range of depths of discharges (20%, 40%, 60%, 80% and 100%) of the cell's theoretical capacity; a range of cathode capacities (1.0, 1.5, 2.0, 2.5 and 3.0 mA h cm<sup>-2</sup>); a range of discharge current densities (0.2, 0.5, 1.0 and 2.0 mA cm<sup>-2</sup>), and different charging techniques (constant current, constant potential and mixed mode). The results of the testing will be presented as a benchmark performance and included in a technical report. The length of cycle testing will be constrained by the testing equipment available.

#### **Work Package 2.**

AEA Technology will study the cycling performance of the Mark I LPB in which  $V_6O_{13}$  is replaced as the active cathode material by:  $LiMn_2O_4$  and related spinels (e.g.  $Li_2Mn_4O_9$ );  $MnO_2$ ;  $V_2O_5$  and  $TiO_2$ . Following initial evaluation of the compounds listed above, AEA Technology will attempt to optimise the Mark I cell configuration and/or composition to yield cycle performance which is superior to that of the  $V_6O_{13}$ -based Mark I cell. The testing and evaluation of these alternative cathode material cells will be restricted to combinations of parameters (i.e. depth of discharge, current density and cathode capacity) for which it is possible to predict superior performance.

#### **Work Package 3.**

AEA Technology will apply several investigative analytical techniques which it has developed, or is in the process of developing, to identify LPB performance limiting phenomena. AEA Technology will build LPB cells which contain a reference terminal and use three terminal

a.c. impedance analysis to monitor changes in the overall cell impedance, the lithium/electrolyte impedance and the electrolyte/cathode impedance during cycling. Using the resulting data AEA Technology will attempt to modify the LPB cell configuration and/or composition to remove or reduce any identified performance limiting factors. AEA Technology will section LPB after testing, and use a scanning electron microscope to examine the physical condition of the cell. EDX analysis will also be used to examine the chemical composition of the cell layers. Using the resulting data AEA Technology will attempt to modify the LPB cell configuration and/or composition to remove or reduce any identified performance limiting factors. AEA Technology will use a post test X-ray diffraction technique to examine the crystal structure of the active cathode material. Using the resulting data AEA Technology will attempt to modify the LPB cell configuration and/or composition to remove or reduce any identified performance limiting factors.

### **1.3 The Current Report**

This report is the third technical report which documents the work performed over the period 1<sup>st</sup> February 1993 to 31<sup>st</sup> March 1993 and is deliverable item 004. The report covers the third two months of effort under Work Package 1, and experiments in Work Package 3.

## 2. Status of Research Effort - Progress against Objectives

### 2.1 Status of Work in Work Package 1

The Mark I LPB cell has been defined as a lithium metal anode, a lithium-ion conducting polymer electrolyte ( $\text{PEO}_{12}:\text{LiClO}_4$ ) and a composite cathode based on  $\text{V}_6\text{O}_{13}$ . A detailed description of the Mark I LPB and the experimental procedures employed in the fabrication of tests cells can be found in the First Technical Report (AEA-InTec-1161).

The initial space power duty cycle agreed for this evaluation project consists of a fixed discharge time of 72 minutes and a total charging time of 10 hours. In order to undertake Task 1.1 a cathode capacity of  $2.5 \text{ mA h cm}^{-2}$  was initially chosen. This gives a theoretical capacity of 100 mA h for the  $40 \text{ cm}^2$  Mark I LPB cell. The discharge current has been varied to correspond to DoDs of 20%, 40%, 60%, 80% and 100% as indicated in Table I below.

Table I

DoD	Discharge current / mA	Current density / mA / $\text{cm}^2$	Discharge rate
20%	16.7	0.42	C/6
40%	33.3	0.83	C/3
60%	50.0	1.25	C/2
80%	66.7	1.67	C/1.5
100%	83.3	2.01	C/1.2

The investigation of the effect of cathode capacity and current density on cycle life, as described in Tasks 1.2 and 1.3 respectively, has been initiated by the fabrication of a 'thin' composite cathode (i.e. capacity  $1.15 \text{ mA h cm}^{-2}$ ) as described in the Second Technical Report (AEA-InTec-1226). The discharge current has been varied to correspond to DoDs of 20%, 40%, 60%, 80% and 100% as indicated in Table II. It should be noted that although the discharge rate for a Mark I LPB cell containing the 'thin' cathode cycling with a particular DoD is the same as for the  $2.5 \text{ mA h cm}^{-2}$  cathode (given in Table I) the current density is lower.



Table II

DoD	Discharge current / mA	Current density / mA / cm <sup>2</sup>	Discharge rate
20%	7.7	0.19	C/6
40%	15.3	0.38	C/3
60%	23.0	0.58	C/2
80%	30.7	0.77	C/1.5
100%	38.3	0.96	C/1.2

In the first sequence of experiments a 'mixed' mode of charging (MT) was selected. This consists of a constant current charge to 3.25 V followed by a potentiostatic hold at 3.25 V such that the total charge time is 10 hours. As part of Task 1.4 two alternative methods of charging, constant current (IT) and constant voltage (VT), have also been evaluated. For the IT mode the charging current was calculated so as to replace the capacity removed during the discharge in a total charge time of 10 hours. Thus the charging rate (and current density) will be significantly lower than the discharge rate, and dependent on the depth of discharge. For example, at 20% depth of discharge the discharge rate is C/6, but the charging rate is only C/50 (i.e. replacing 20% of the theoretical capacity in 10 hours). A lower voltage limit of 1.5 V has been used to determine the end of life in all cases.

The cycle performance data are presented in two forms; discharge energy versus cycle number and end of discharge voltage versus cycle number.

A summary of the cell testing performed in Work Package 1 in the first six months of the project is given in Table III. Although a number of these cycling experiments are still in progress several trends in performance have already been identified. The results are presented first for the standard 2.5 mA h cm<sup>-2</sup> capacity cathode and then for the 'thin' 1.15 mA h cm<sup>-2</sup> capacity cathode.

Table III

Summary of cell testing performed in Work Package 1 to date

2.5 mA h cm<sup>-2</sup> capacity cathode (standard)

DoD	MT	IT	VT
20%	√*R	√*	√
40%	√	√*	√
60%	√	√	
80%	√	√	√
100%	√	√	√

1.15 mA h cm<sup>-2</sup> capacity cathode ('thin')

DoD	MT	IT	VT
20%	√*R	√*	
40%	√	√*	
60%	√*	√*	
80%	√	√*	
100%			

\* - indicates testing in progress.

R - indicates a repeat experiment.

### 2.1.1 Performance with Cathode Capacity of $2.5 \text{ mA h cm}^{-2}$

#### Mixed Mode Charging

The cycling performance data for a group of three Mark I LPB cells (P069, P070 and P071) discharged to 20% depth of discharge using a mixed mode charge are given in Figure 2. The energy loss over the first 80 cycles is of the order of four percent, with a more rapid decline during subsequent cycles. The maximum cycle life for the Mark I LPB cell under a 20% depth of discharge and a mixed mode charge is approximately 120 cycles. Experiments designed to determine the cause of cell failure show cell impedance values at the end of test, Figure 3, have undergone a large increase when compared to the initial cell impedance values ( $< 1 \Omega$ ). This was a repeat of an earlier experiment terminated after 90 cycles due to a cycling rig crash (LPB cells P003, P004 and P005, see page 11 of the Second Technical Report).

Figure 4 shows the cycling performance data for 2 Mark I LPB cells (P074 and P075) discharged to 40% depth of discharge using a mixed mode charge. Cell testing was terminated after 72 cycles following a rapid decline in both output energy and end of discharge voltage. This was a repeat of the original experiment performed on LPB cells P007, P009 and P010 (see page 14 of the Second Technical Report). Again cell failure was due to a build-up in total cell impedance.

Figure 5 illustrates a direct comparison between the performance data for the Mark I LPB with a cathode capacity of  $2.5 \text{ mA h cm}^{-2}$ , at 20% (P069), 40% (P075) and 60% (P012) depth of discharge cycling under the specified duty cycle with a mixed mode method of charging. The cycle life is clearly a function of depth of discharge; the greater the depth of discharge the higher the energy output each cycle, but for fewer cycles. Under this particular testing regime cycle life is limited to a maximum of 120 cycles as observed for 20% depth of discharge. The limitation in cycle life is a direct result of a resistance increase within the cell, which appears to accelerate during the 5-10 cycles before failure.

#### Constant Current Charging

The cycling performance data for two Mark I LPB cells discharged to 20% depth of discharge and charged with a constant current for ten hours are shown in Figure 6. The LPB cells P078 and P079 have performed 110 and 105 cycles respectively, and remain on test. The energy loss over the first 100 cycles was approximately four percent. A comparison with the cells which employ a mixed mode charging technique, Figure 7, indicates that the use of constant current charging results in an apparent improvement in the longer term cycling performance at 20% depth of discharge. This will be confirmed over the next few weeks.

Figure 8 shows the cycling performance data for a group of three Mark I LPB cells discharged to 40% depth of discharge and charged with constant current. These LPB cells have performed 70 cycles and remain on test. During the first 20 cycles the energy loss of 3.5% was approximately twice that observed for LPB cells cycled at 40% depth of discharge with a mixed mode charge. However, a comparison of the cycling performance data, Figure 9, demonstrates the superior energy output obtained from the LPB cells charged with constant current after 40 cycles.

The cycling performance data for two Mark I LPB cells discharged to 60% depth of discharge and charged with constant current are given in Figure 10. The LPB cells P091 and P092 failed after 53 and 13 cycles respectively. The variability exhibited by these two cells has been observed in earlier experiments and has been attributed to the hand construction methods currently employed. A comparison with the mixed mode of charging, Figure 11, provides further evidence of the enhancement in performance that can be obtained by the use of a constant current charging method.

Figure 12 illustrates the cycling performance as a function of depth of discharge using a constant current charge. Although previous experience, on cycling to 100% depth of discharge, suggested the use of a constant current charge may result in an unacceptable level of capacity decline, particularly during the initial cycles, this has not proved to be the case for lower depths of discharge. The performance data as defined by end of discharge voltage for LPB cells cycling with a constant current charge show an initial drop and a recovery. This becomes more apparent with higher depths of discharge, and is believed to be partially due to a structural rearrangement within the  $V_6O_{13}$ . However, for lower depths of discharge the effect is negligible and the overall advantage of a mixed mode charge is lost. The cycling data for 20% and 40% depth of discharge has demonstrated the performance improvement of constant current charging over that of the mixed mode. At the present time constant current appears to be the most desirable method of charging the Mark I LPB cell.

### **Constant Voltage Charging**

The conclusion on the use of a ten hour constant voltage charge, as described in the Second Technical Report, was that it appeared to be detrimental to the long term cycling of the Mark I LPB cell. No further cycling performance evaluations using constant voltage charging have been carried out in this reporting period and this method of charging has been eliminated from consideration.

#### **2.1.2 Performance with Cathode Capacity of $1.15 \text{ mA h cm}^{-2}$**

The energy output (energy density) from LPB cells with a 'thin' capacity cathode  $1.15$

$\text{mA h cm}^{-2}$  is proportionally lower than that obtained from LPB cells containing the standard  $2.5 \text{ mA h cm}^{-2}$  cathode (described above) cycling under the same conditions. Therefore the only justification for changing to a thin cathode in the Mark I LPB cell is the demonstration of a performance improvement in terms of depth of discharge and cycle life. At this point in the project the cell testing on LPB cells containing the 'thin' cathode is at a less advanced stage than that of the standard  $2.5 \text{ mA h cm}^{-2}$  capacity cathode as indicated in Table III.

Figure 13 shows the initial cycling performance data for two LPB cells discharged to 20% depth of discharge with a mixed mode charge. This is a repeat of the original experiment (LPB cells P041, P042 and P044), discussed in the Second Technical Report, where some differences in cycling behaviour were observed at the point when the testing was terminated. The present LPB cells P093 and P094 have performed 70 cycles and remain on test.

The cycling performance data for two LPB cells discharged to 60% depth of discharge with a mixed mode charge are given in Figure 14. These LPB cells have performed 40 cycles and remain on test. Although the cycle life of these cells is already greater than that measured for the  $2.5 \text{ mA h cm}^{-2}$  cathode cycling under the same 60% depth of discharge conditions, in view of the earlier results it appears unlikely that the maximum will exceed that of 100 observed for the 'thin' cathode cycling at 40% depth of discharge reported previously.

The initial cycling performance data for a LPB cell, P083, discharged to 80% depth of discharge with a mixed mode charge, Figure 15, demonstrates the good utilisation of the active cathode material at a high discharge rate ( $C/1.5$ ). A comparison of the first discharge curve of P083 with that of P032 containing a  $2.5 \text{ mA h cm}^{-2}$  capacity cathode, Figure 16, illustrates the improved rate performance of a LPB cell with the thinner cathode, sustaining the discharge current for the required 72 minutes. P083 performed 36 cycles before failure.

One consequence of the use of constant current rather than mixed mode charging is a performance improvement observed for the LPB cells containing a  $2.5 \text{ mA h cm}^{-2}$  capacity cathode and one might expect a similar result for LPB cells with the  $1.15 \text{ mA h cm}^{-2}$  cathode. The initial cycling performance data obtained for 20% and 40% depth of discharge with a constant current charge, Figures 17 and 18, show a rather large degree of variability within groups of cells tested under the same conditions. These LPB cells and those discharging at 60% and 80% depth of discharge (only recently initiated) remain on test. Further cycling data is required before any conclusion can be drawn concerning the possible performance benefits of using a 'thin' cathode in the Mark I LPB cell.

## 2.2 Status of Work in Work Package 3

The purpose of Work Package 3 is to identify and understand the performance limitations of the Mark I LPB, or subsequent improvements, thereby enabling a reduction or removal of any

such limiting factors. This Work Package will employ three analytical techniques; post-test SEM/EDX analysis, three terminal a.c. impedance and post test X-ray diffraction studies, and is designed to run in parallel with the LPB cell cycling experiments performed in Work Packages 1 and 2.

Many of the results from Work package 1 indicate that a build-up of cell impedance is the major performance limiter of the Mark I LPB. As part of Task 3.1 three terminal a.c. impedance studies have been initiated in order to establish whether the origin of this impedance build-up is: i) occurring in the electrolyte layer, ii) the result of an interfacial resistance on one or both of the electrode surfaces, or iii) occurring within the bulk of the composite cathode. The inclusion of a thin lithium reference electrode within the polymer electrolyte (total of 4 layers) of the Mark I LPB cell provides a means of separating the contributions of the anode and cathode interfacial impedances.

The three terminal LPB cell P085 (cathode capacity  $2.5 \text{ mA h cm}^{-2}$ ) was cycled at 60% depth of discharge with a mixed mode charge. This LPB cell performed 14 cycles before the test was terminated due to the cell failing to discharge for the required 72 minutes. The overall cell impedance, together with the anode and cathode contributions, after 2 and 13 cycles, are given in Figures 19 and 20 respectively. In each case the overall impedance corresponds to the sum of the anode and cathode values. It should be noted that the scales on these impedances plots are not all the same but are selected in such a way that the individual impedance contributions can be most clearly seen. After 13 cycles a significant increase in the overall cell impedance had occurred as a result of increases in both anode and cathode interfacial resistances. The cathode contribution appeared larger than that of the anode.

The three terminal LPB cell P106 (cathode capacity  $2.5 \text{ mA h cm}^{-2}$ ) was cycled at 40% depth of discharge with a mixed mode charge. This LPB cell remains on test. The initial impedance values are shown in Figure 21. A comparison with the impedance measurements taken after 8 and 28 cycles, Figures 22 and 23, indicate a slight decrease in the overall cell impedance primarily as a result of a decrease in the anode contribution. The reduction of the anode interfacial resistance during the initial cycles may result from the removal of a surface film originally present on the metallic lithium surface, or simply signify a reduction in the contact resistance of the polymer electrolyte/lithium anode interface.

The Mark I LPB cell P075 cycled at 40% depth of discharge with a mixed mode charge performed 72 cycles before failure, as shown in Figure 4. The a.c. impedance of P075 at the end of test, Figure 24, indicated an increase in the cell resistance compared to the initial value. This LPB cell has been investigated using a cryogenic sectioning technique (described in the Second Technical Report) that enables the individual layers of the laminated cell structure to be examined. Figures 25 and 26 show scanning electron micrographs of the cross-section of two different regions of LPB cell P075. Although the individual component layers can still be easily

distinguished there appears to be a degree of disruption within the electrolyte layer, including the presence of several voids. These voids were not observed in the cross-section of the uncycled LPB cell and their origin is currently under investigation. No visual evidence of dendritic growth was observed. Figures 27 and 28 show the polymer electrolyte/composite cathode and polymer electrolyte/lithium interfaces in greater detail.

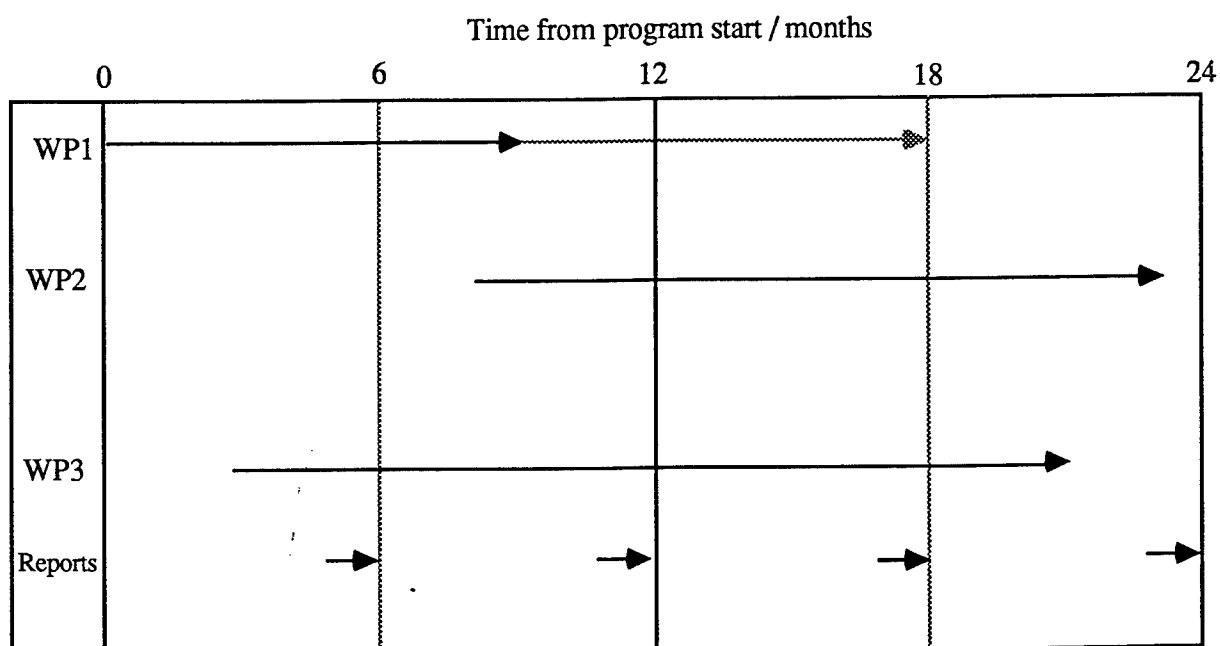
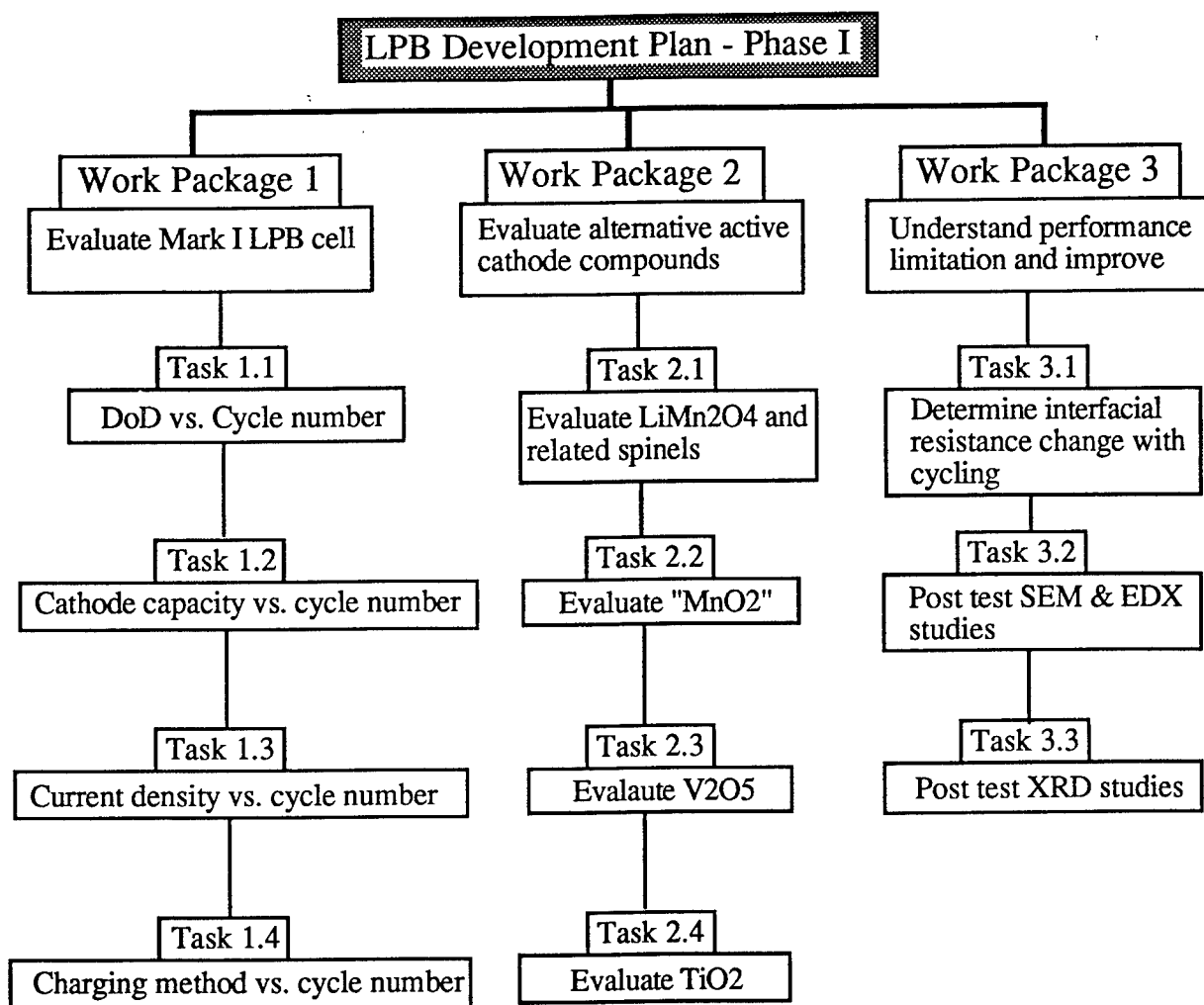
## 2.3 Conclusions

For a Mark I LPB (cathode capacity of  $2.5 \text{ mA h cm}^{-2}$ ) tested under a space power duty cycle consisting of a 72 minute discharge and 10 hour mixed mode charge, the maximum cycle life is approximately 120 cycles for 20% depth of discharge. For 40% and 60% depths of discharge this reduced to 75 cycles and 30 cycles respectively. The use of constant current charging has demonstrated a performance improvement over the mixed mode at 20%, 40% and 60% depth of discharge. Mark I LPB cells cycling at 20% and 40% depth of discharge with a constant current charge have performed 110 cycles and 70 cycles and remain on test. Figure 29 shows that the projected energy densities for optimised Mark I LPB cells under these cycling conditions are approximately 50 and  $100 \text{ W h kg}^{-1}$  for 20% and 40% depth of discharge respectively. The values relate to an unpackaged LPB cell.

**Based on these results, constant current charging can therefore be considered the preferred method in the present space power duty cycle.**

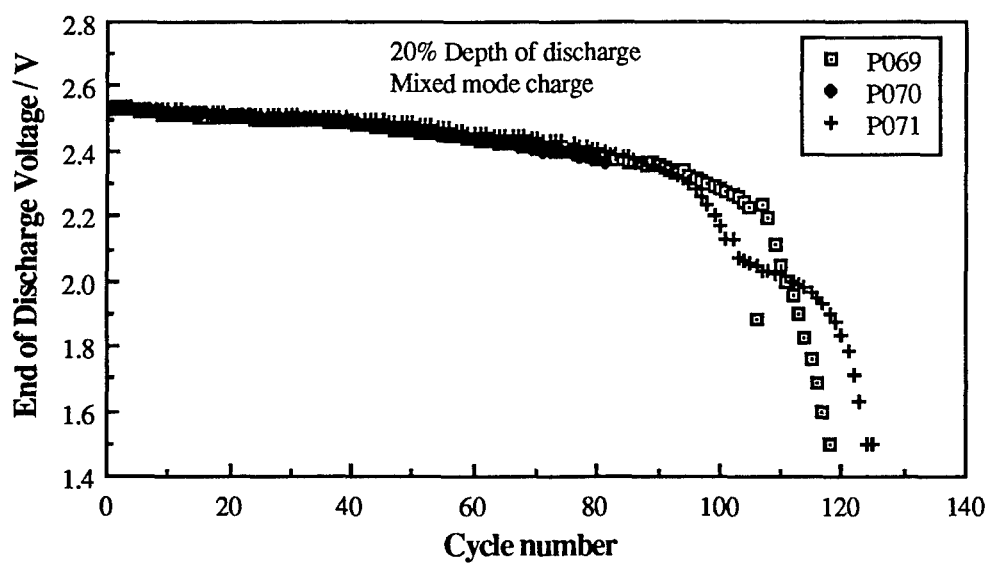
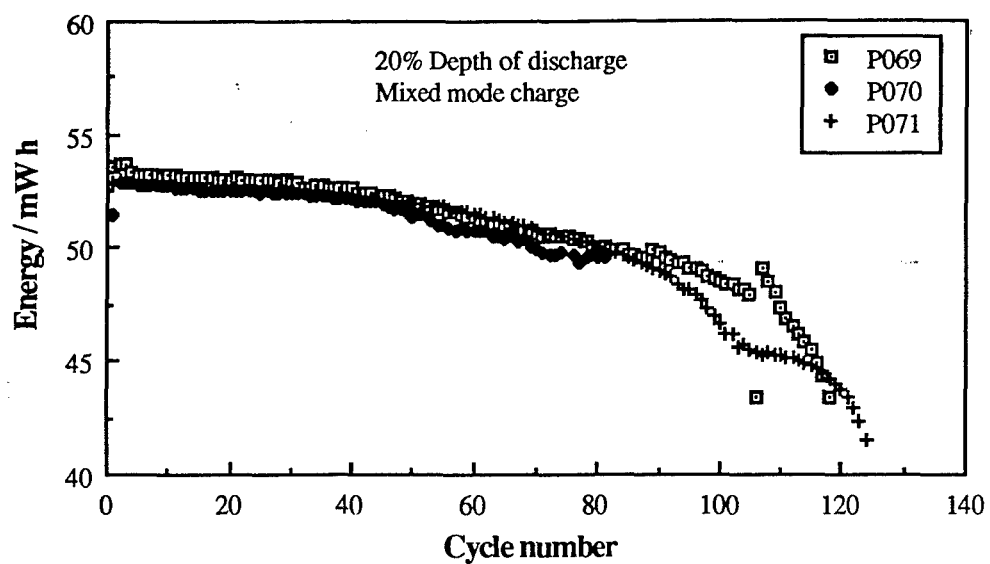
The replacement of the  $2.5 \text{ mA h cm}^{-2}$  capacity cathode with a 'thin' capacity electrode,  $1.15 \text{ mA h cm}^{-2}$ , will result in reduction on the energy density of the Mark I LPB cell for a given depth of discharge. Therefore LPB cells containing the 'thin' capacity cathode must exhibit a level of performance at say 40% depth of discharge that exceeds that shown by the LPB cells with a standard  $2.5 \text{ mA h cm}^{-2}$  capacity cathode cycling at 20% depth of discharge. Although the use of a 'thin' capacity cathode  $1.15 \text{ mA h cm}^{-2}$  in the Mark I LPB cell has led to a performance improvement over the  $2.5 \text{ mA h cm}^{-2}$  capacity cathode in terms of rate capability, as demonstrated by the 80% depth of discharge cycling, additional cycling data is required to determine whether there will be any performance enhancement by extending cycle life.

The rapid cell failure observed for the Mark I LPB cycling at 60% depth of discharge with a mixed mode charge has been identified with an increase in cell impedance. Three terminal a.c. impedance measurements indicate this build-up in resistance is primarily cathode-related, and therefore may be associated, at least in part, with the  $\text{V}_6\text{O}_{13}$  cathode material. It is therefore possible that performance improvements can be achieved with the use of alternative active cathode materials such as those based on manganese or titanium oxides.

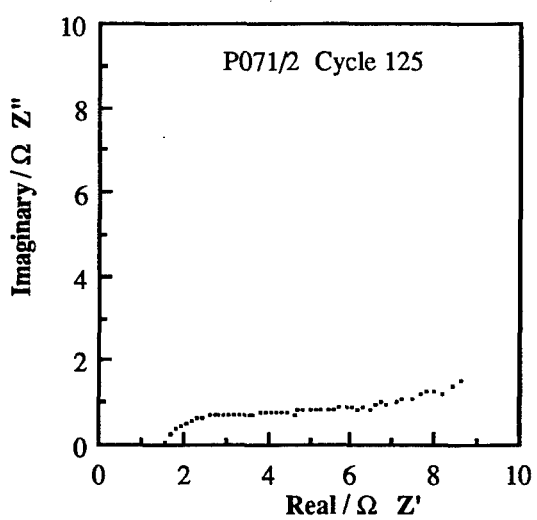
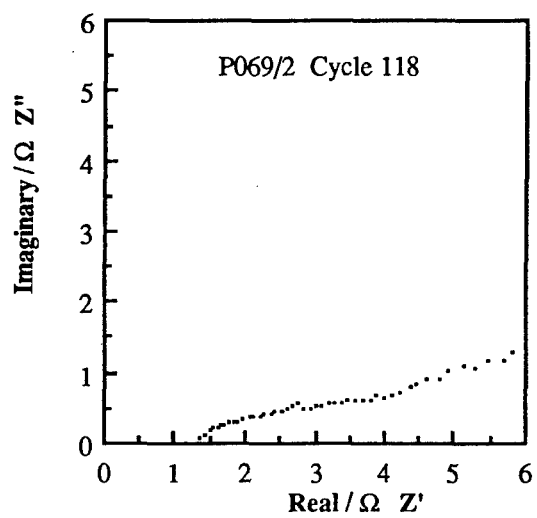


**Figure 1 Work Breakdown Structure**

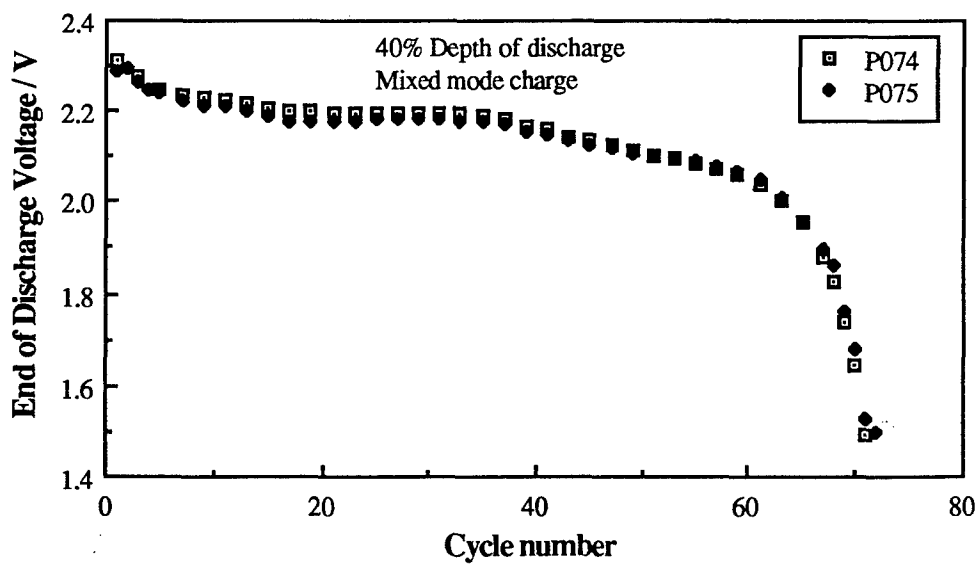
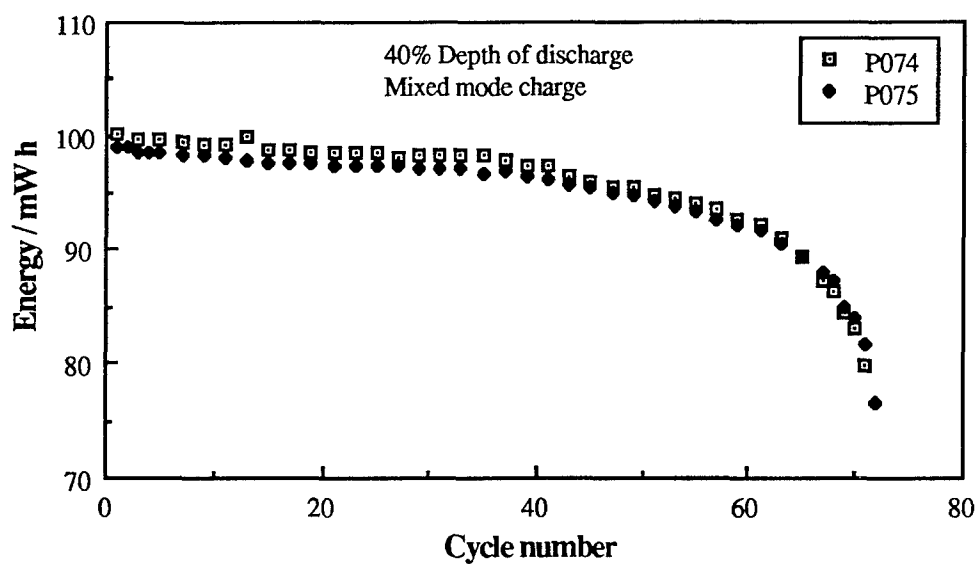




**Figure 2** Cycle performance data for the Mark I LPB cell with a  $2.5 \text{ mA h cm}^{-2}$  capacity cathode at 20% depth of discharge and a mixed mode charge.



**Figure 3** A.c. impedance data for cycled LPB cells P069 and P071.



**Figure 4** Cycle performance data for the Mark I LPB cell with a  $2.5 \text{ mA h cm}^{-2}$  capacity cathode at 40% depth of discharge and a mixed mode charge.

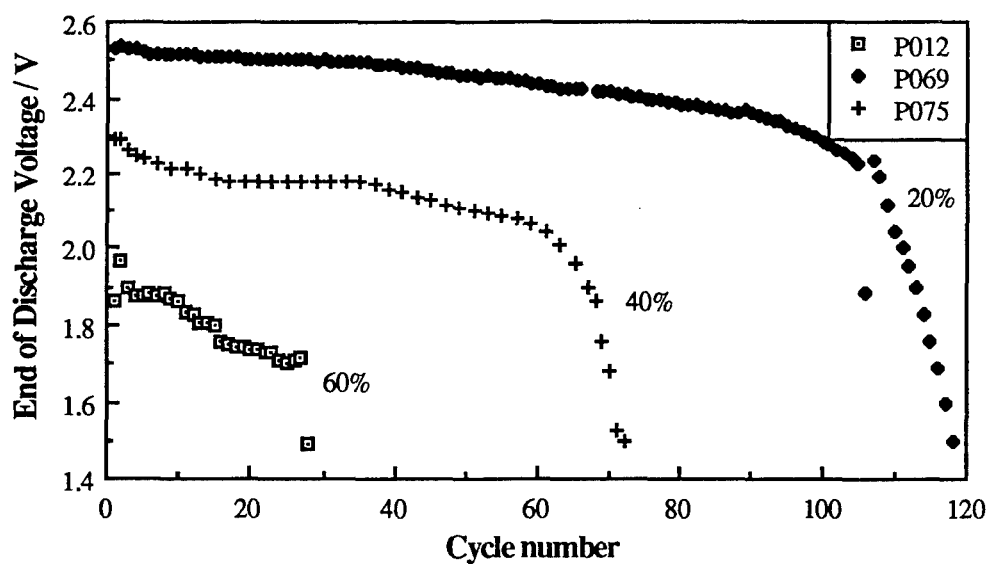
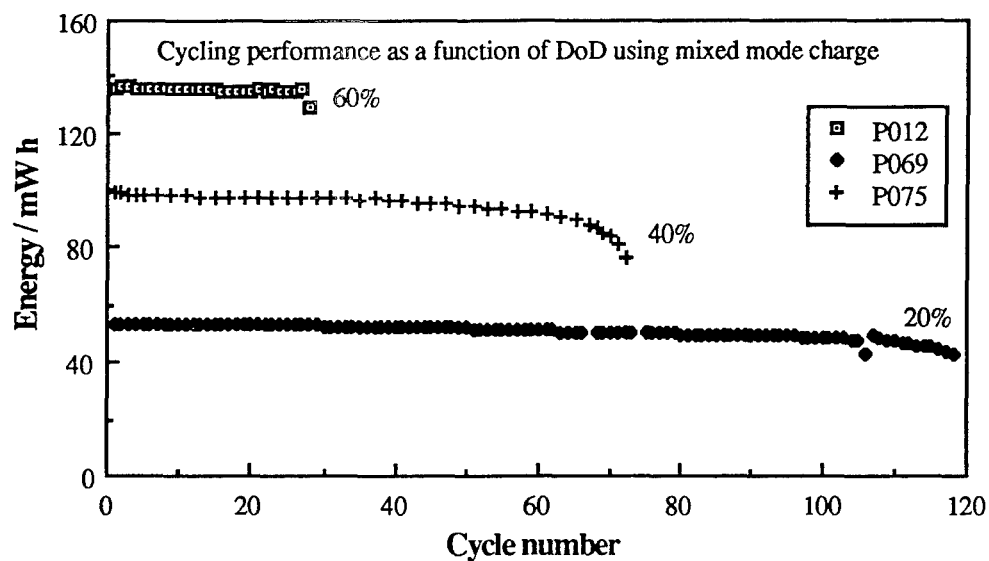
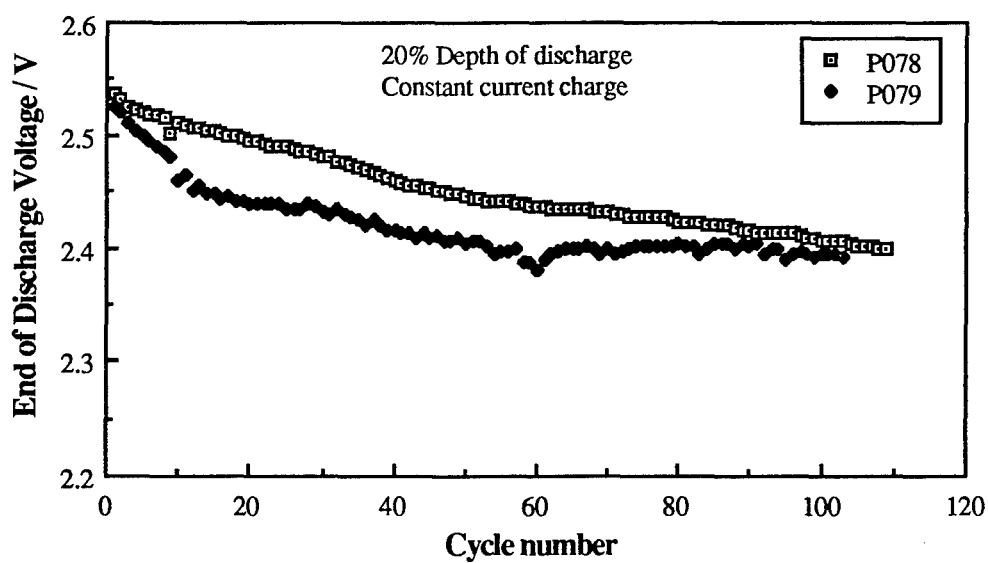
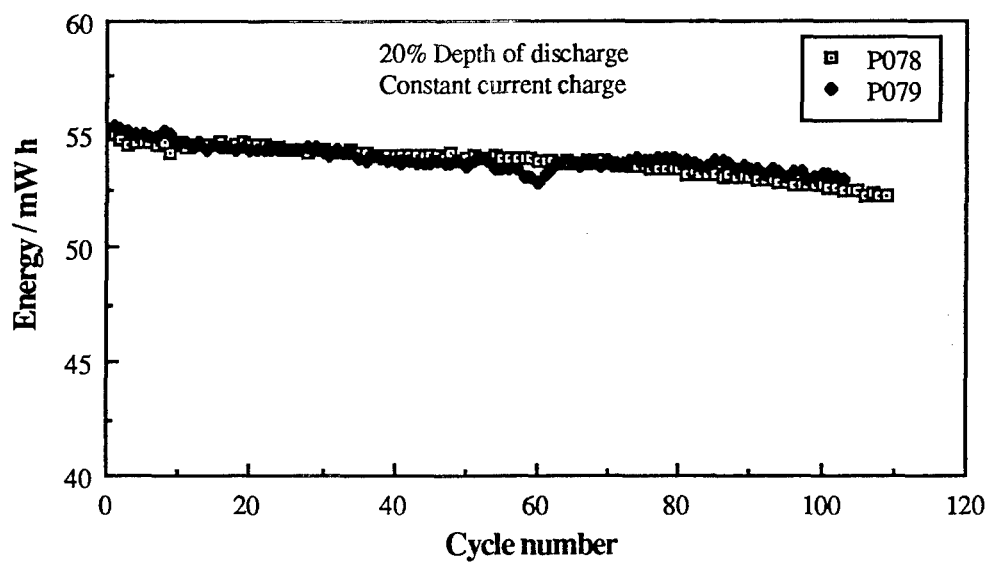
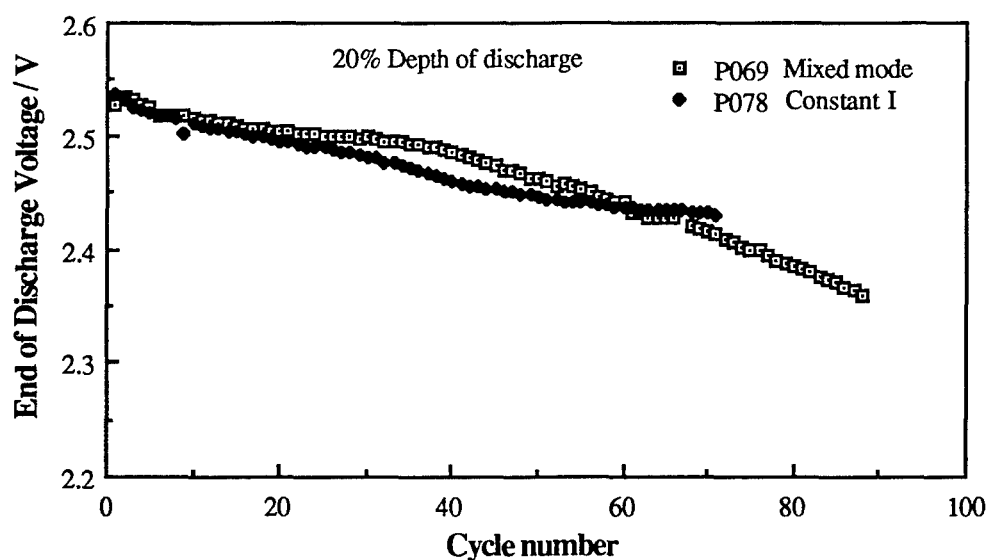
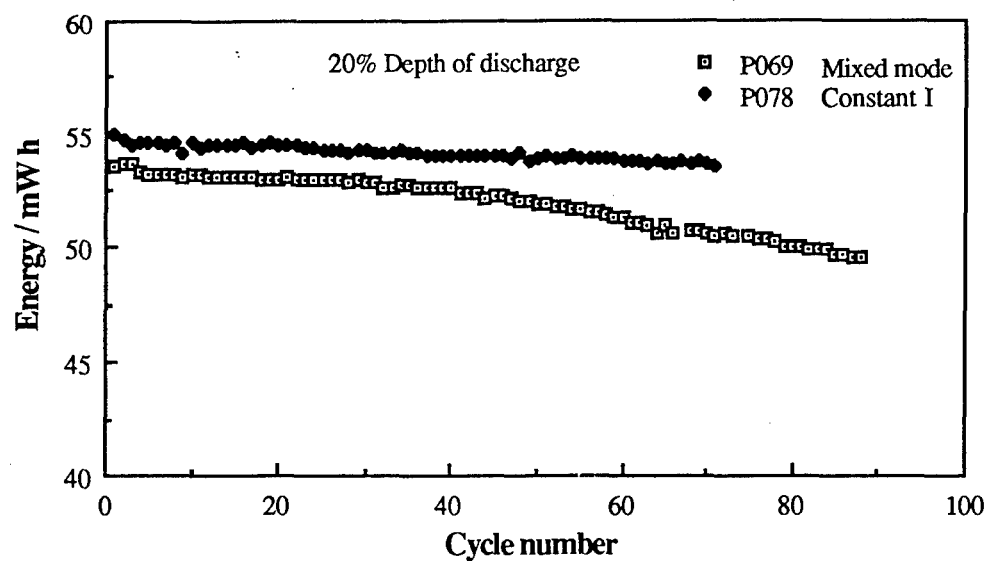


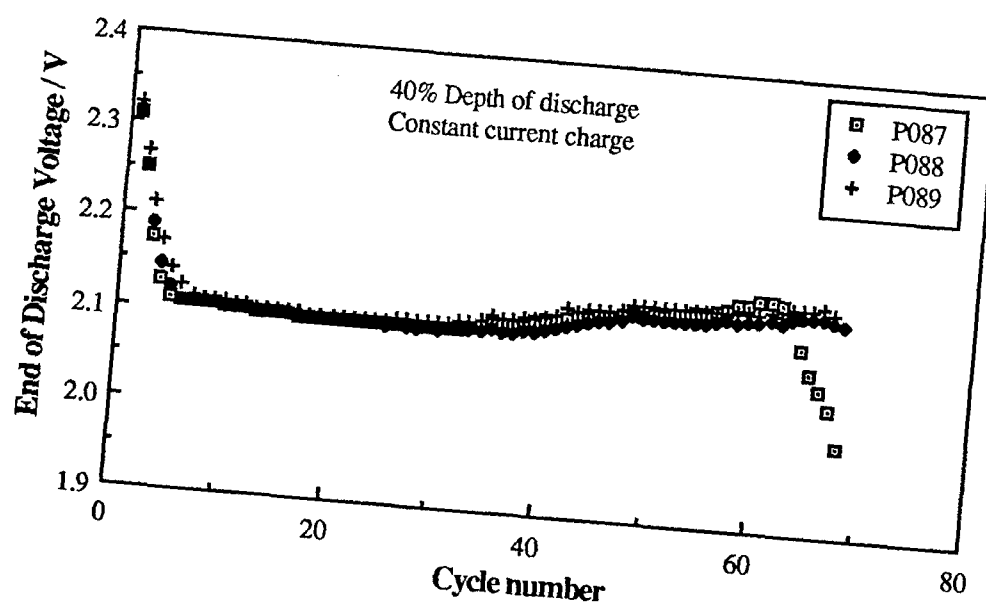
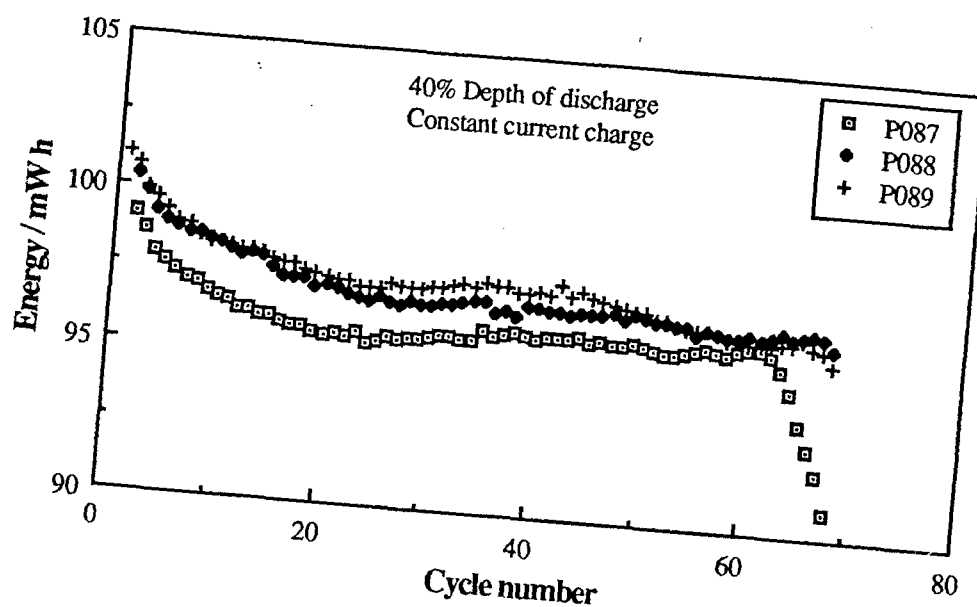
Figure 5 Cycling performance data for the Mark I LPB cell with a  $2.5 \text{ mA h cm}^{-2}$  capacity cathode as a function of depth of discharge using a mixed mode charge.



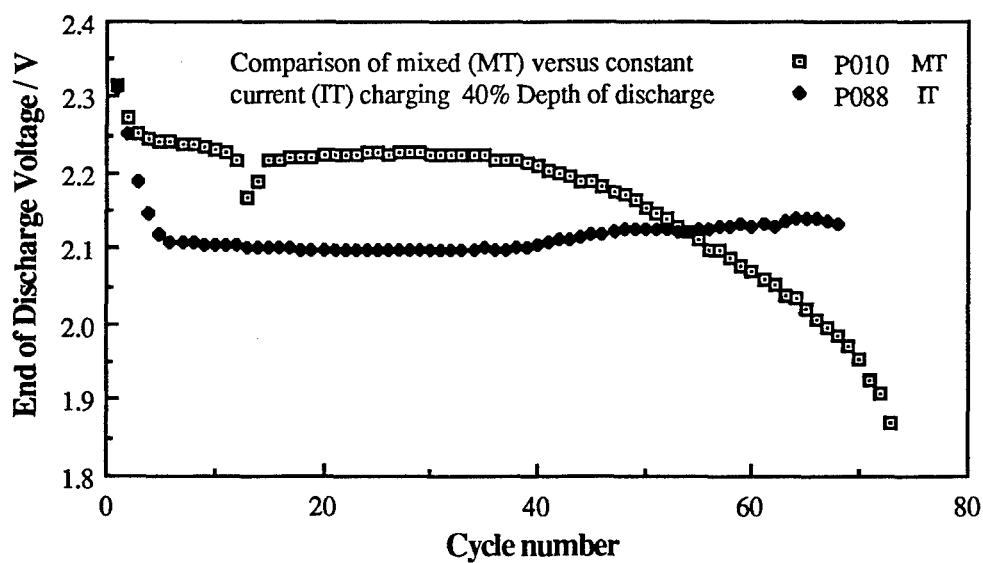
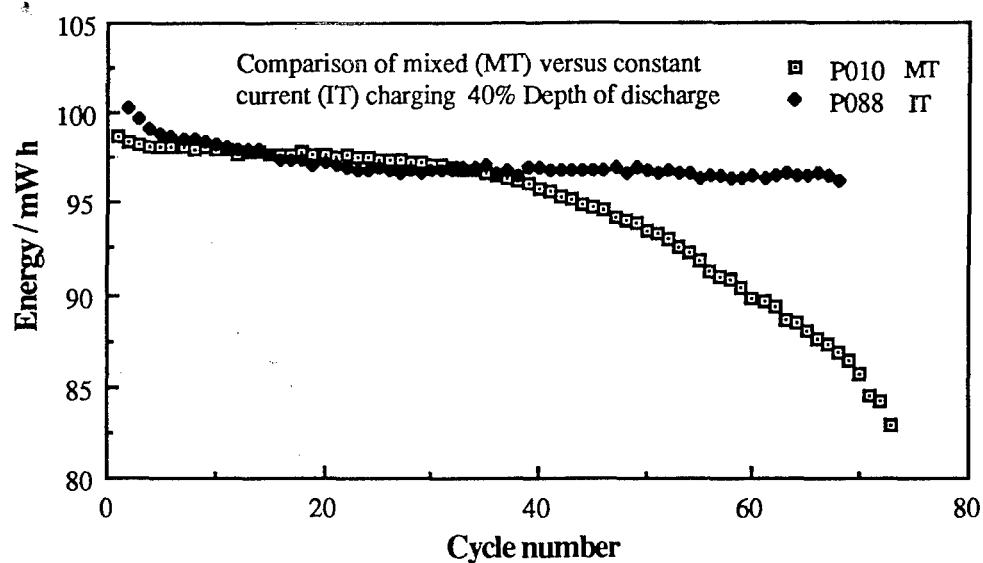
**Figure 6** Cycle performance data for the Mark I LPB cell with a  $2.5 \text{ mA h cm}^{-2}$  capacity cathode at 20% depth of discharge and a constant current charge.



**Figure 7** Comparison of cycle performance data for mixed mode and constant current charging for the Mark I LPB cell with a  $2.5 \text{ mA h cm}^{-2}$  capacity cathode at 20% depth of discharge.

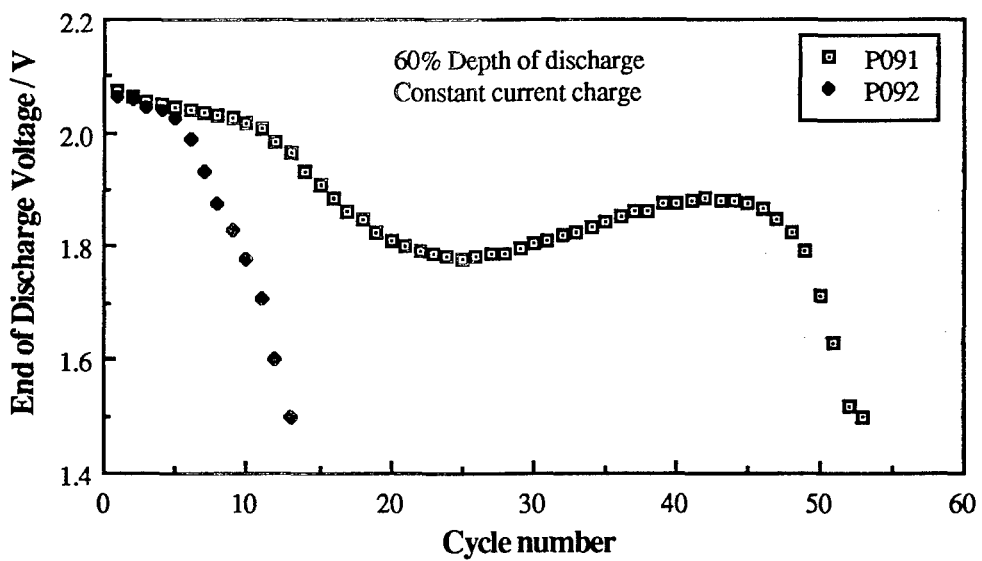
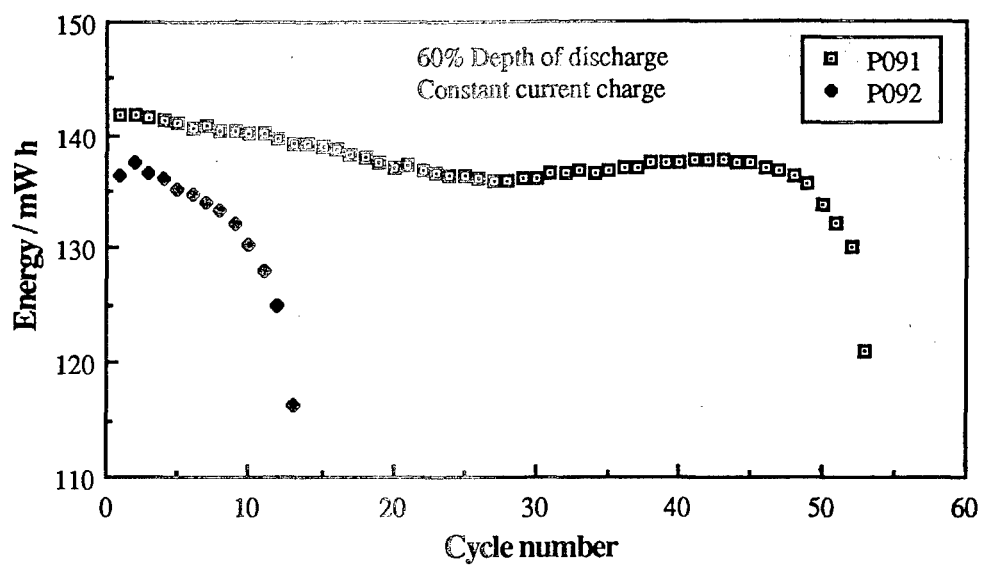


**Figure 8** Cycle performance data for the Mark I LPB cell with a  $2.5 \text{ mA h cm}^{-2}$  capacity cathode at 40% depth of discharge and a constant current charge.

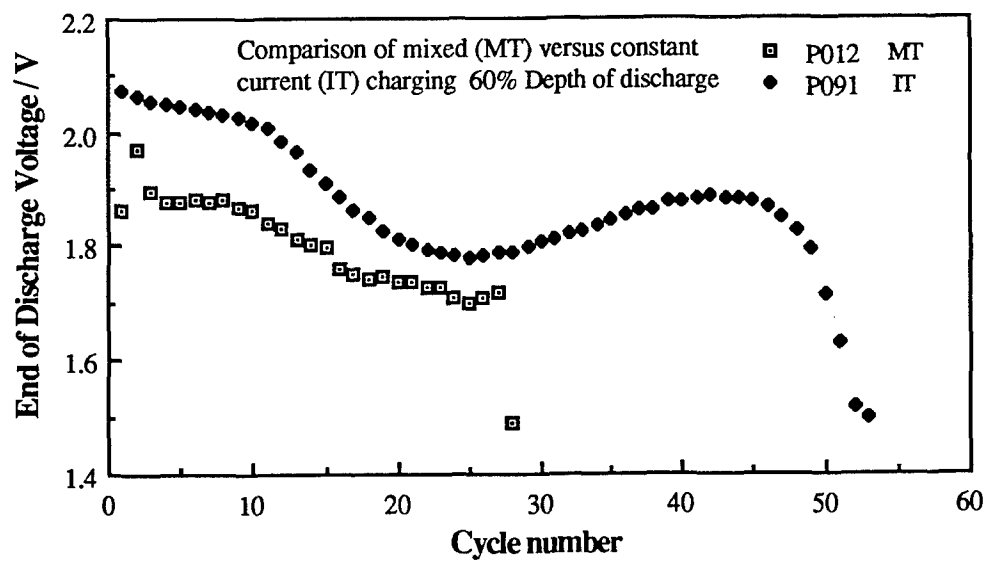
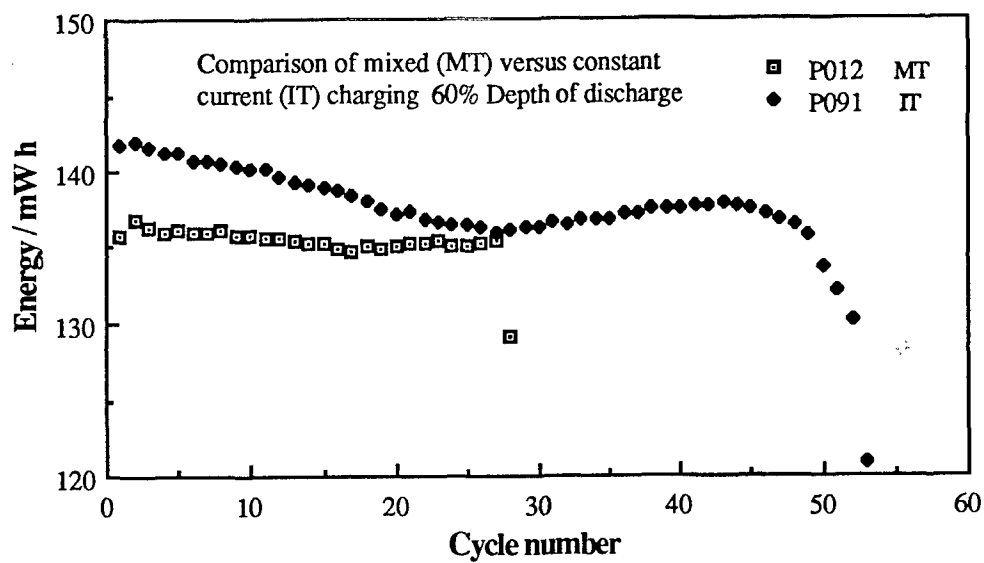


**Figure 9** Comparison of cycle performance data for mixed mode and constant current charging for the Mark I LPB cell with a  $2.5 \text{ mA h cm}^{-2}$  capacity cathode at 40% depth of discharge.





**Figure 10** Cycle performance data for the Mark I LPB cell with a  $2.5 \text{ mA h cm}^{-2}$  capacity cathode at 60% depth of discharge and a constant current charge.



**Figure 11** Comparison of cycle performance data for mixed mode and constant current charging for the Mark I LPB cell with a  $2.5 \text{ mA h cm}^{-2}$  capacity cathode at 60% depth of discharge.

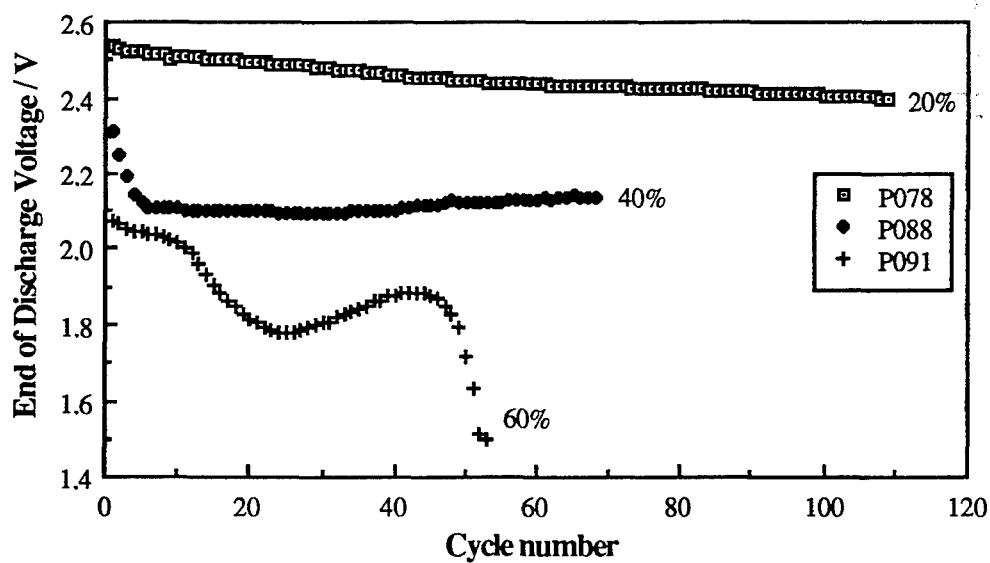
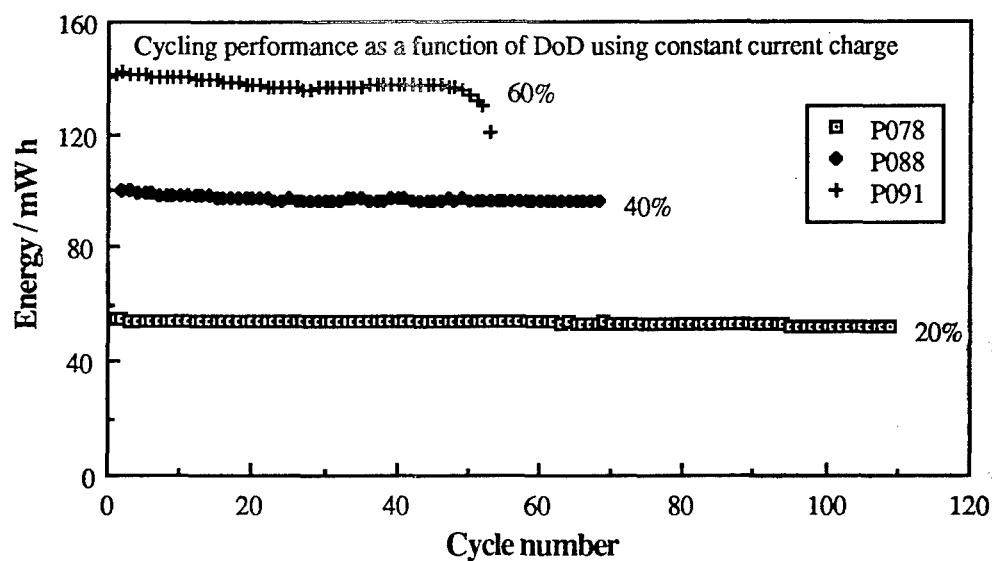


Figure 12 Cycling performance data for the Mark I LPB cell with a  $2.5 \text{ mA h cm}^{-2}$  capacity cathode as a function of depth of discharge using a constant current charge.

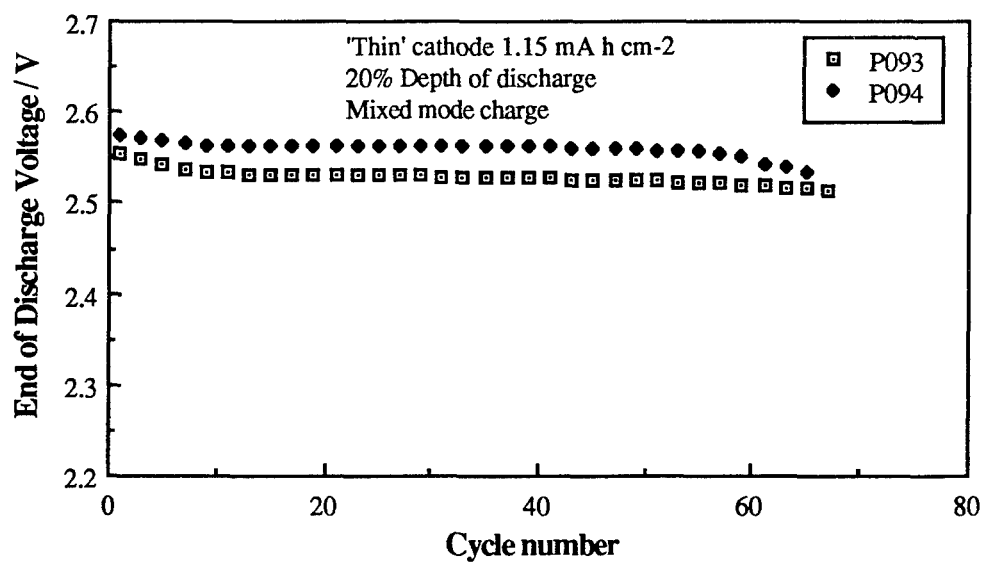
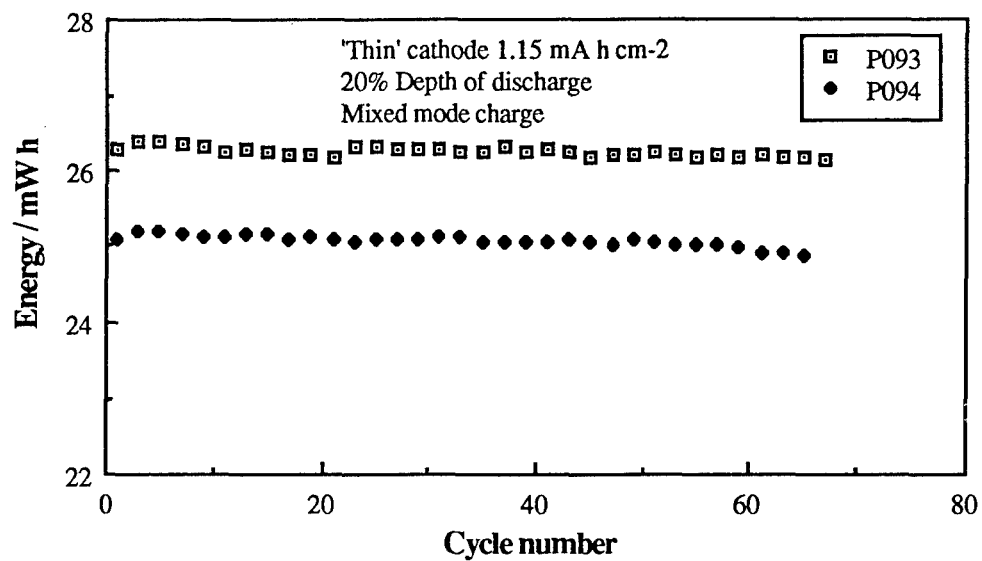


Figure 13 Cycle performance data for the Mark I LPB cell with a 'thin' 1.15 mA h cm<sup>-2</sup> capacity cathode at 20% depth of discharge and a mixed mode charge.

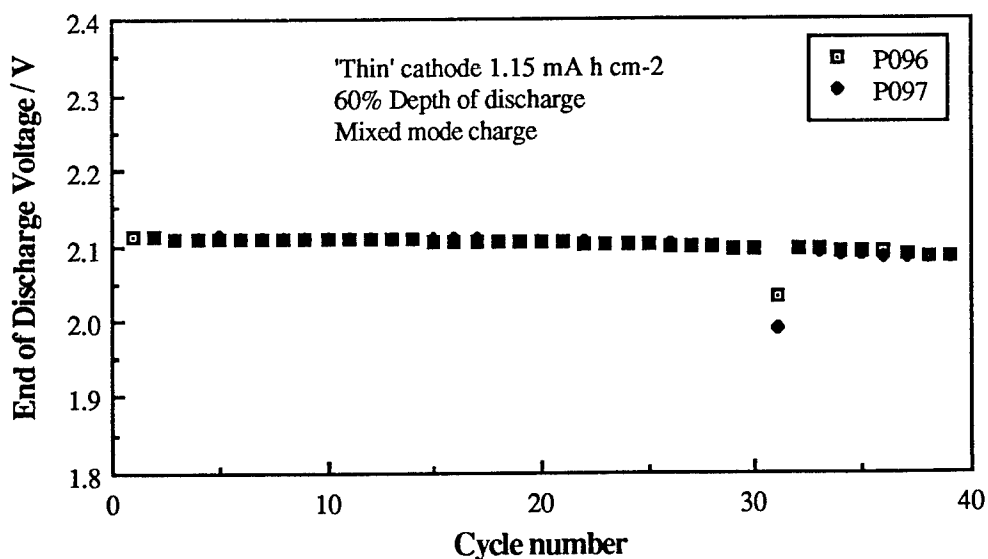
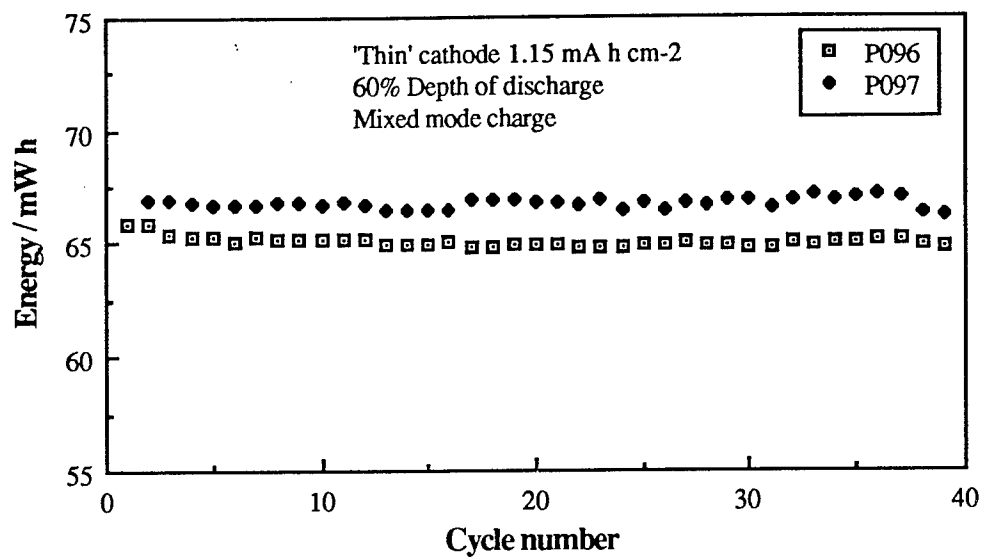


Figure 14 Cycle performance data for the Mark I LPB cell with a 'thin'  $1.15 \text{ mA h cm}^{-2}$  capacity cathode at 60% depth of discharge and a mixed mode charge.

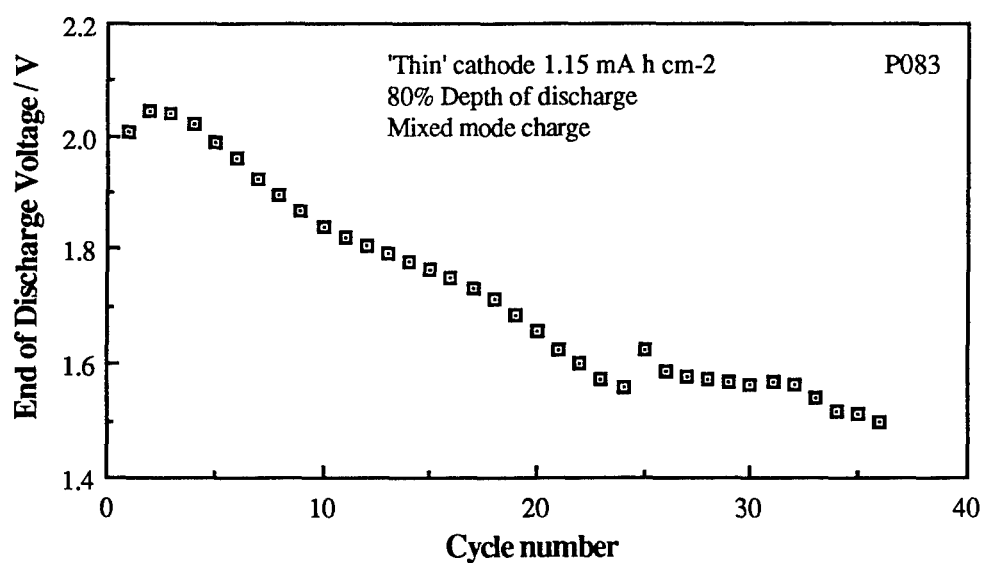
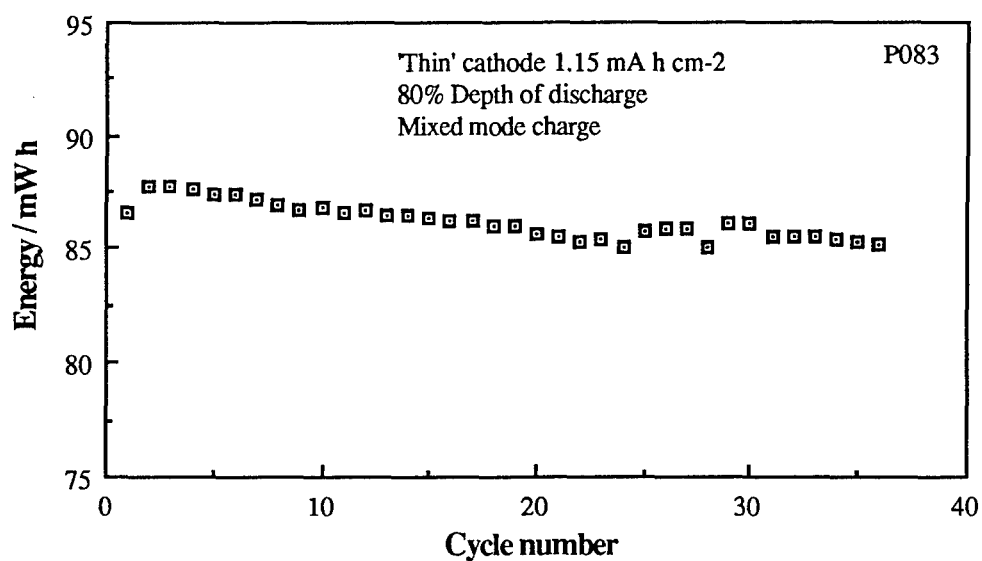
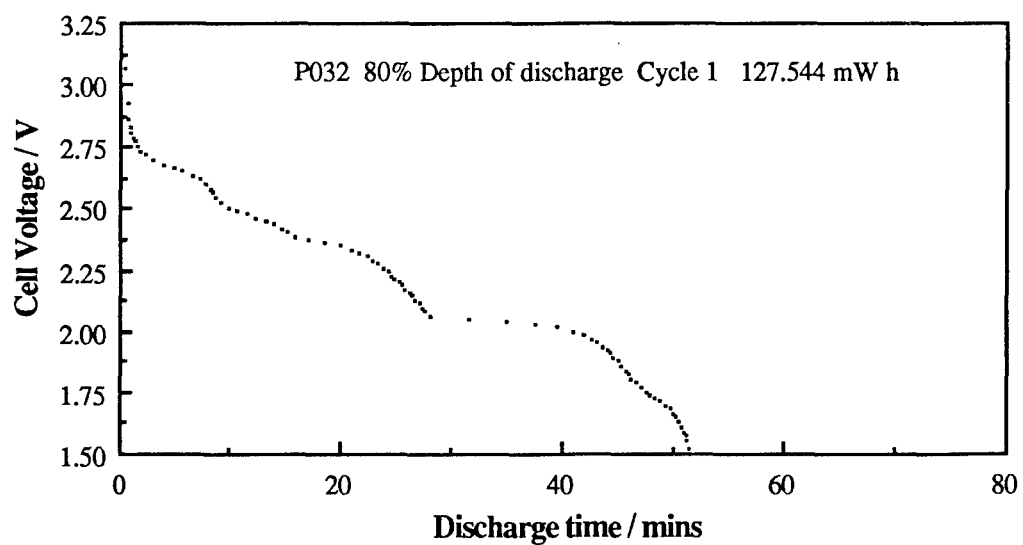
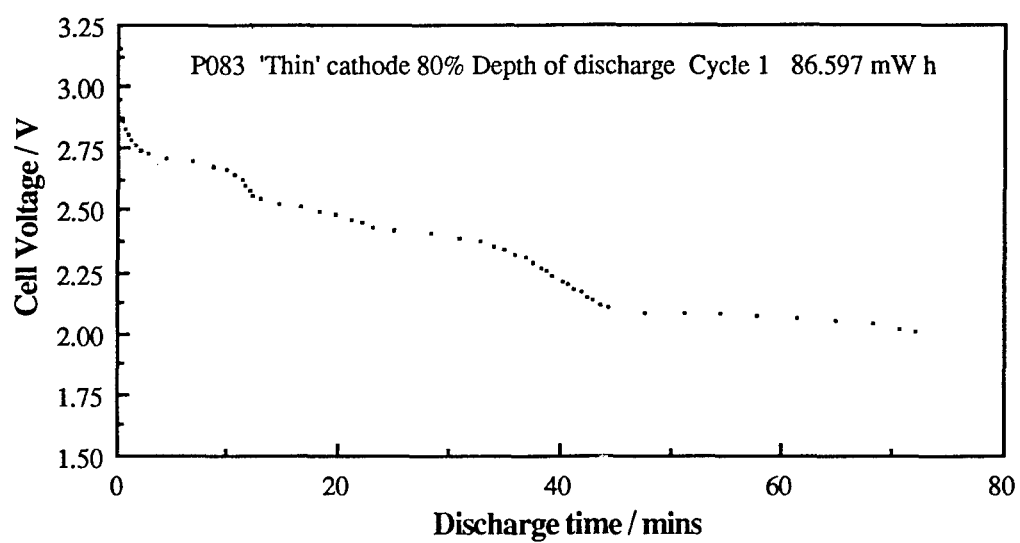
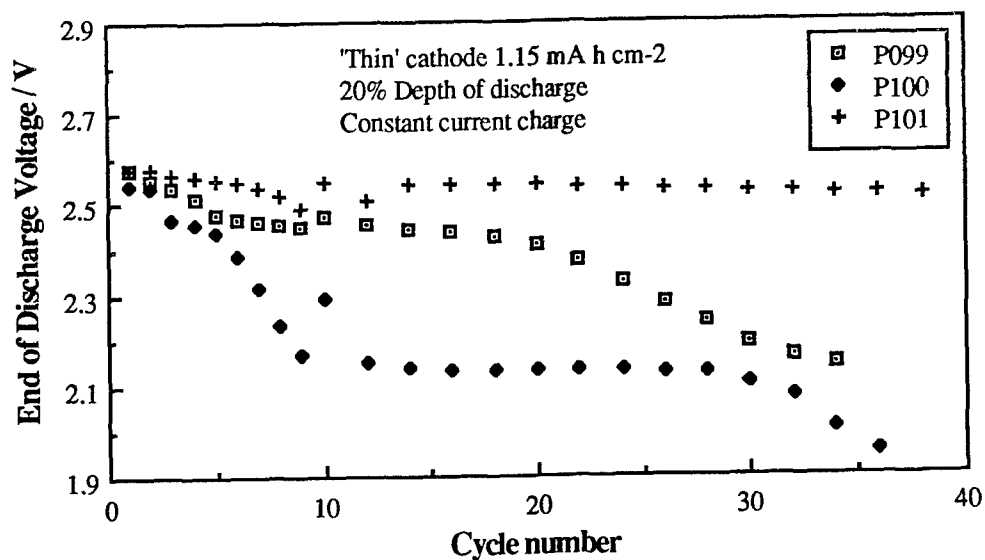
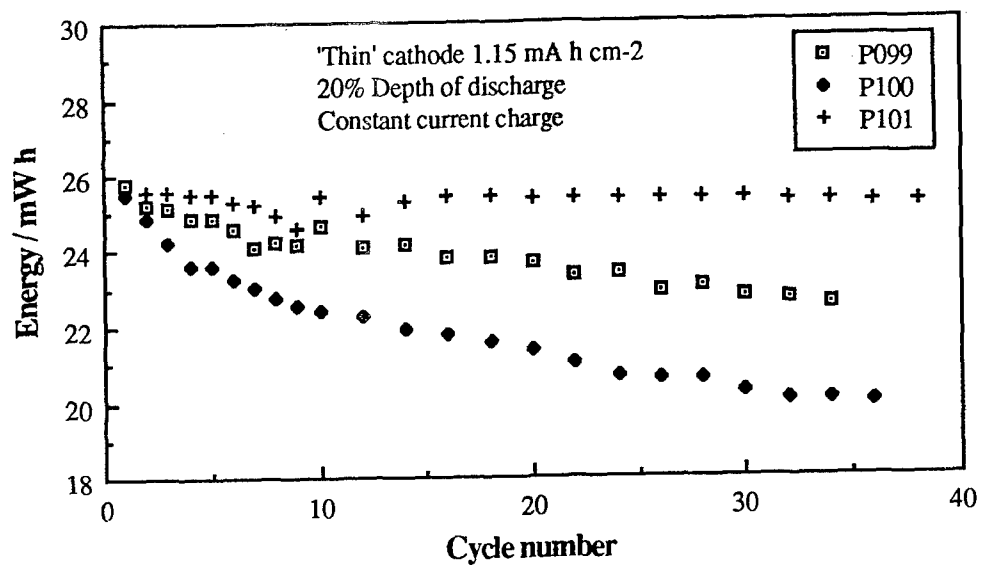


Figure 15 Cycle performance data for the Mark I LPB cell with a 'thin' 1.15 mA h cm<sup>-2</sup> capacity cathode at 80% depth of discharge and a mixed mode charge.

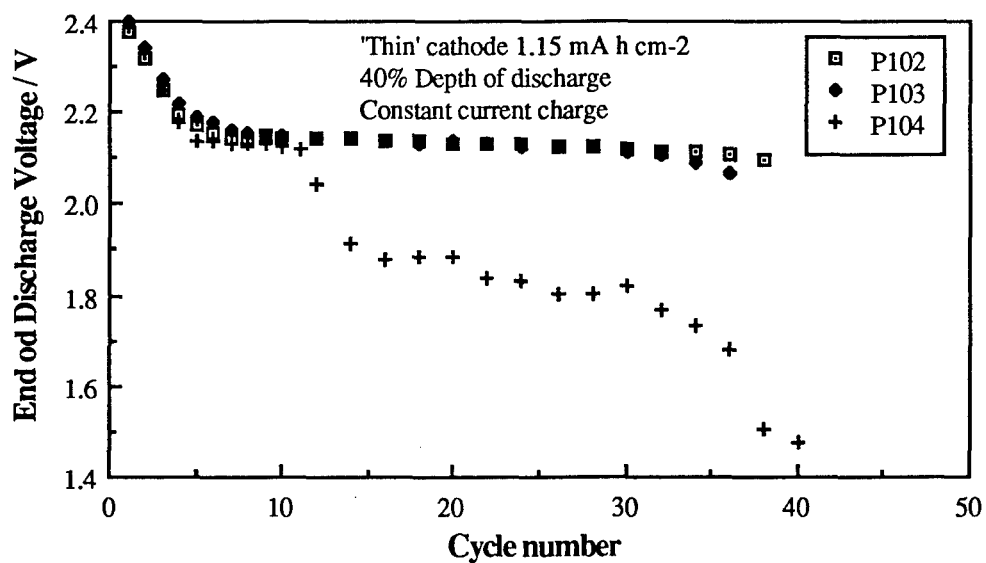
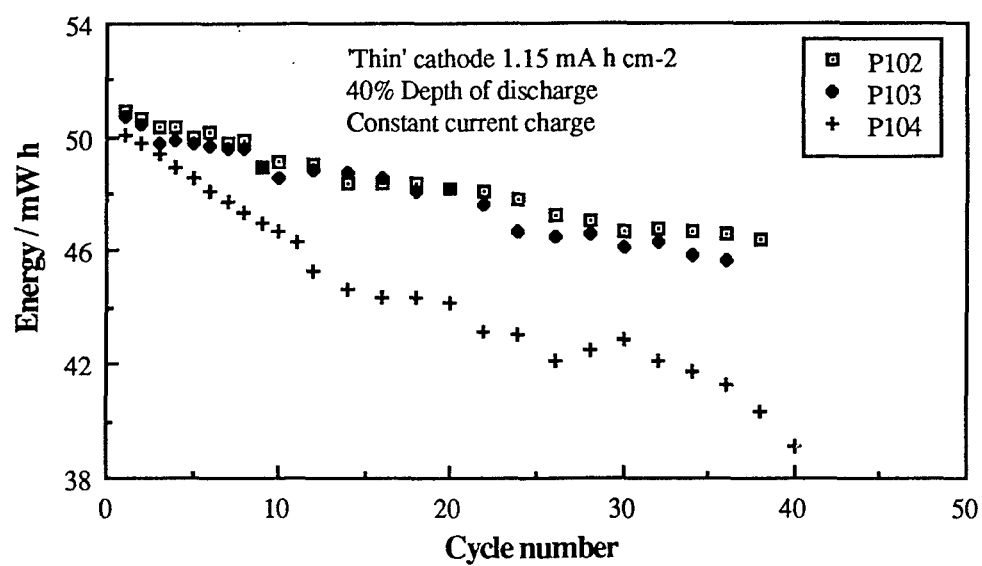


**Figure 16** First discharge data for Mark I LPB cells with 'thin'  $1.15 \text{ mA h cm}^{-2}$  and  $2.5 \text{ mAh cm}^{-2}$  capacity cathodes at 80% depth of discharge.



**Figure 17** Cycle performance data for the Mark I LPB cell with a 'thin'  $1.15 \text{ mA h cm}^{-2}$  capacity cathode at 20% depth of discharge with a constant current charge.





**Figure 18** Cycle performance data for the Mark I LPB cell with a 'thin' 1.15 mA h cm<sup>-2</sup> capacity cathode at 40% depth of discharge with a constant current charge.

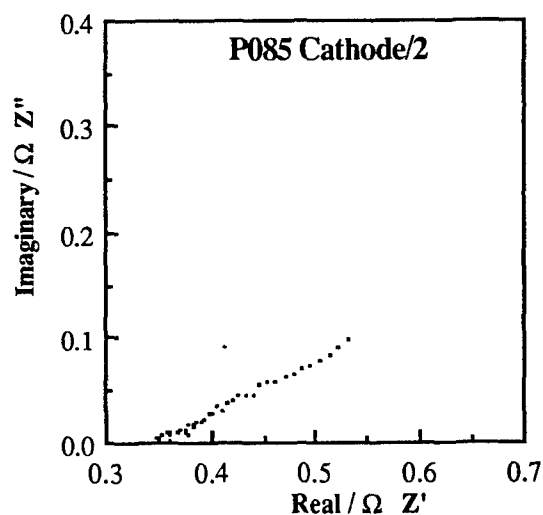
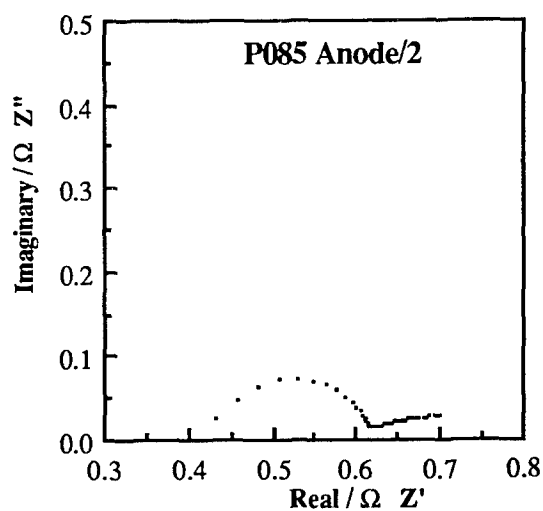
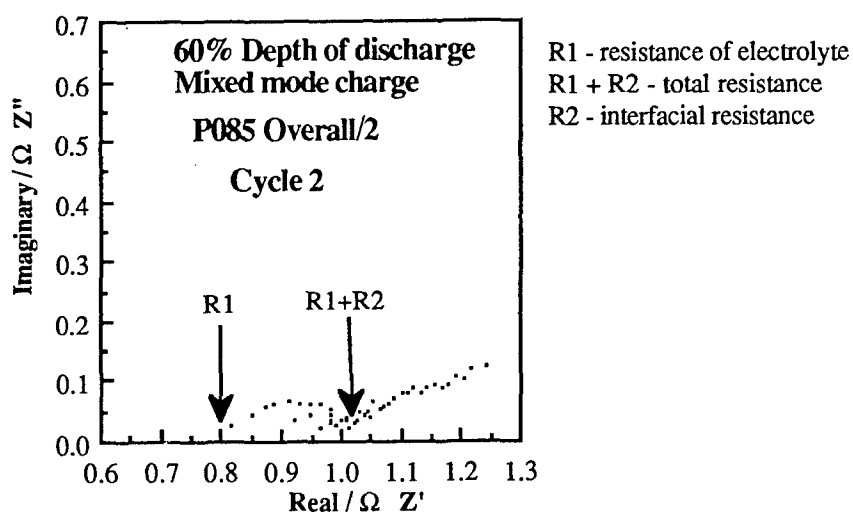
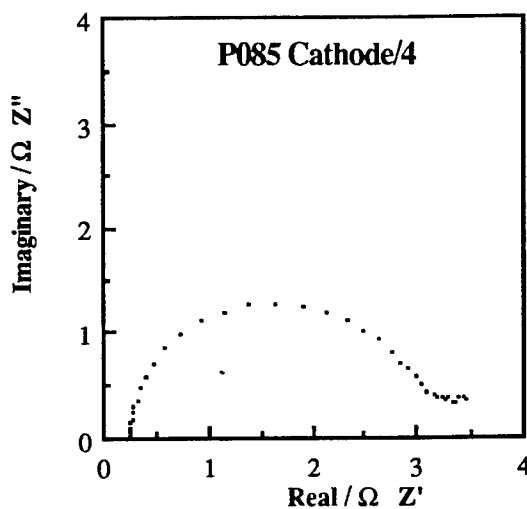
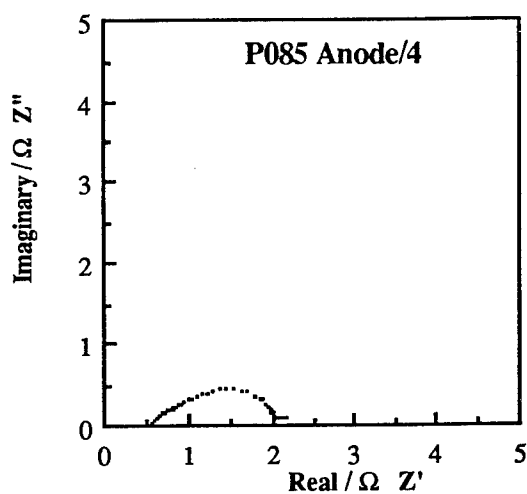
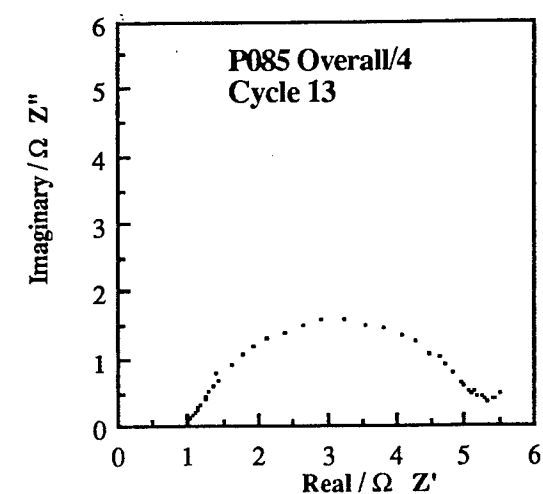
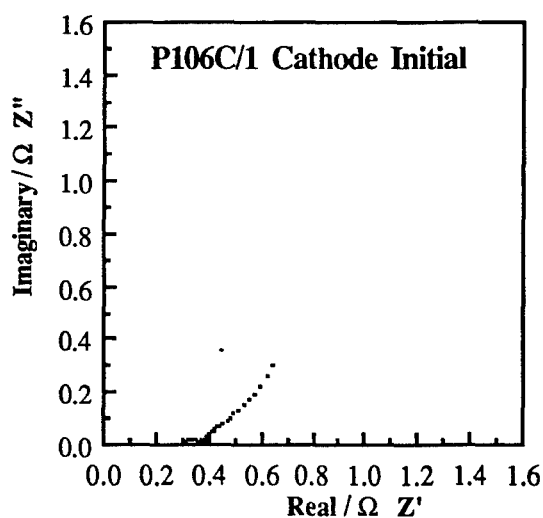
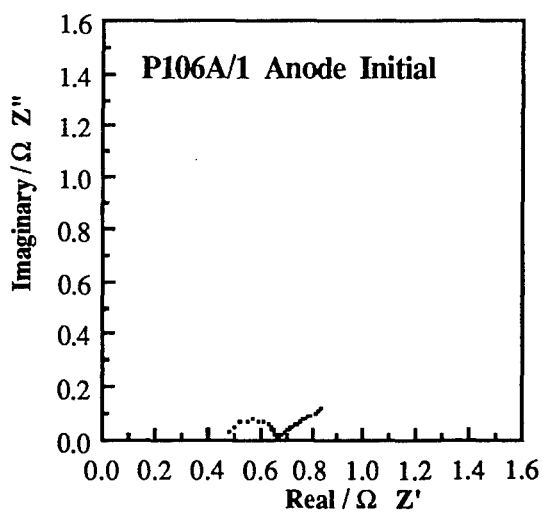
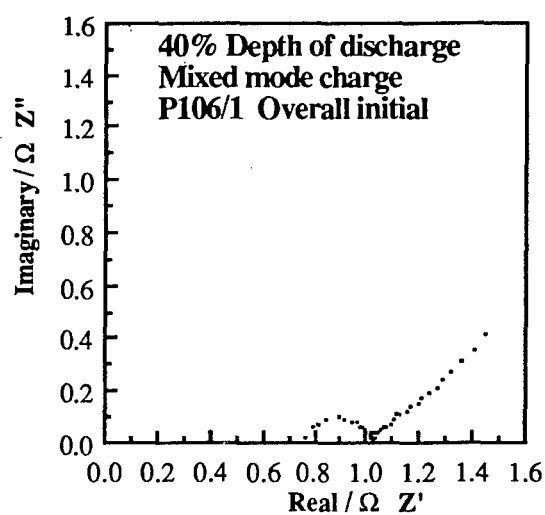


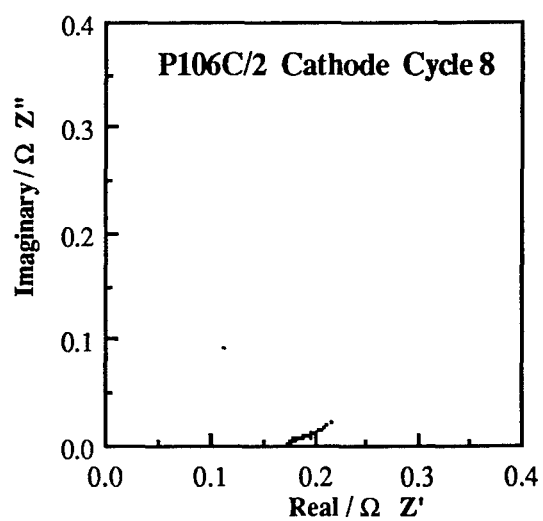
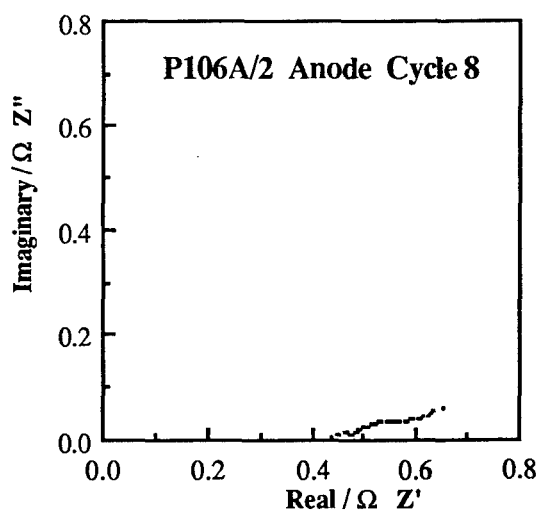
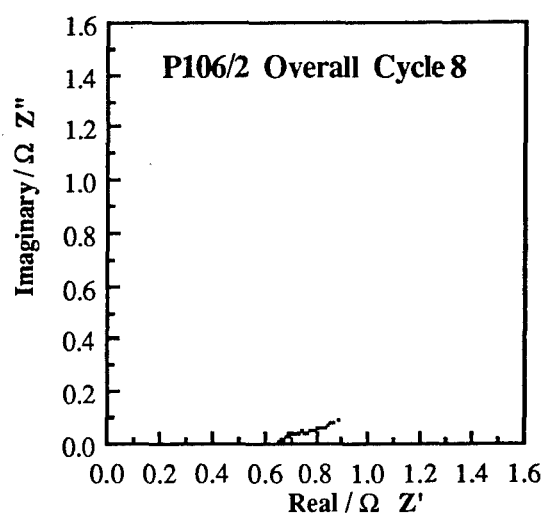
Figure 19 A.c. impedance data after 2 cycles for Mark I LPB cell P085 cycling at 60% depth of discharge with a mixed mode charge.



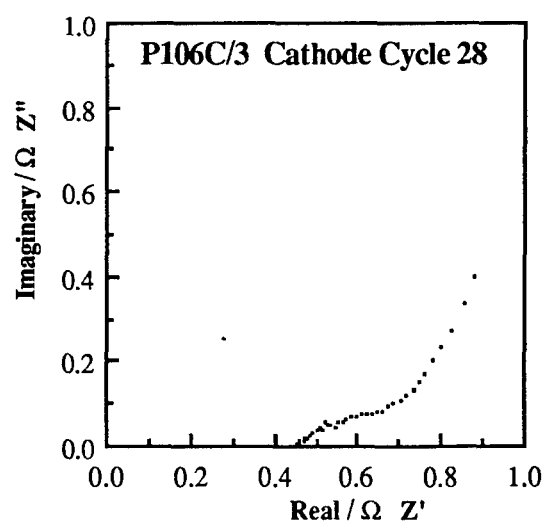
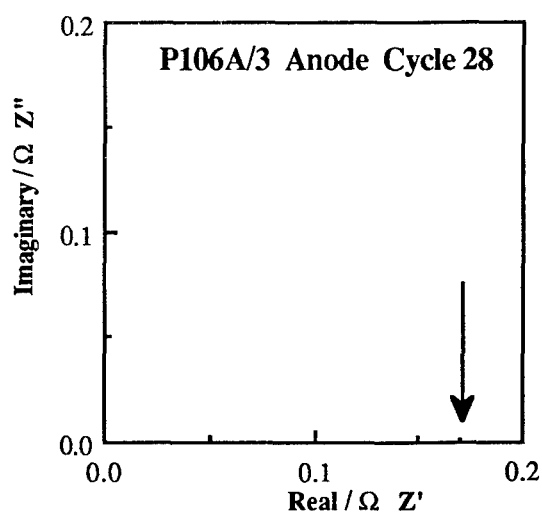
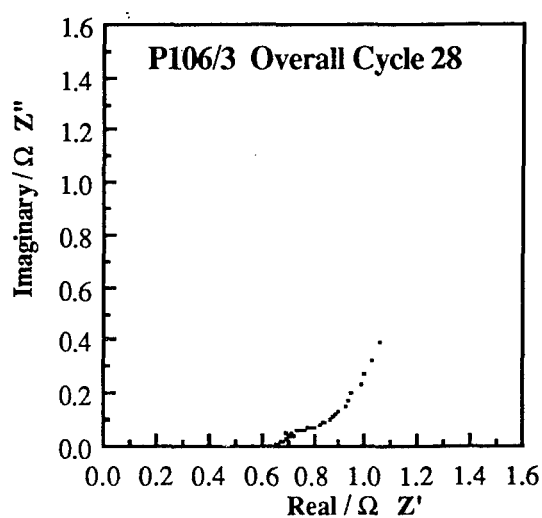
**Figure 20** A.c. impedance data after 13 cycles for Mark I LPB cell P085 cycling at 60% depth of discharge with a mixed mode charge.



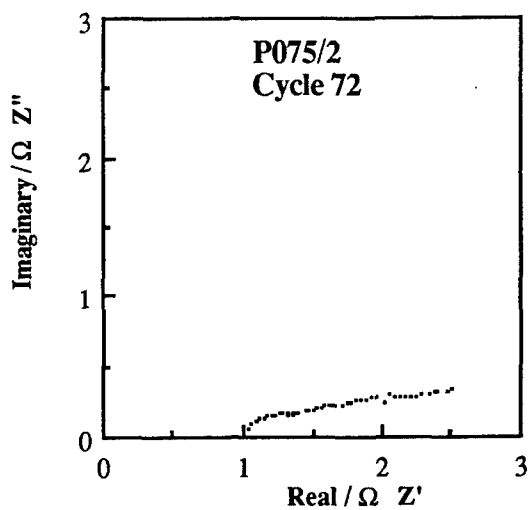
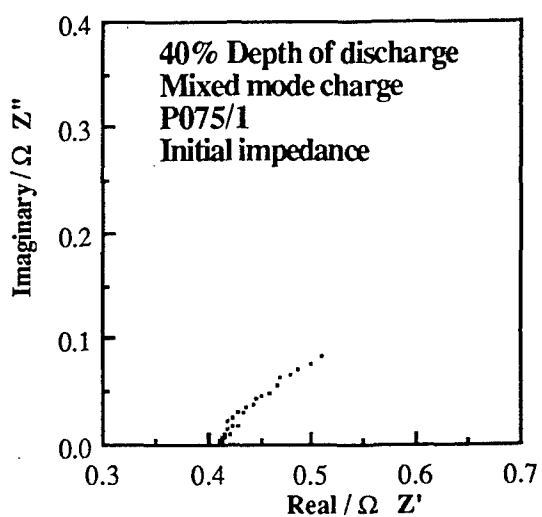
**Figure 21** Initial a.c. impedance data for Mark I LPB cell P106 cycling at 40% depth of discharge with a mixed mode charge.



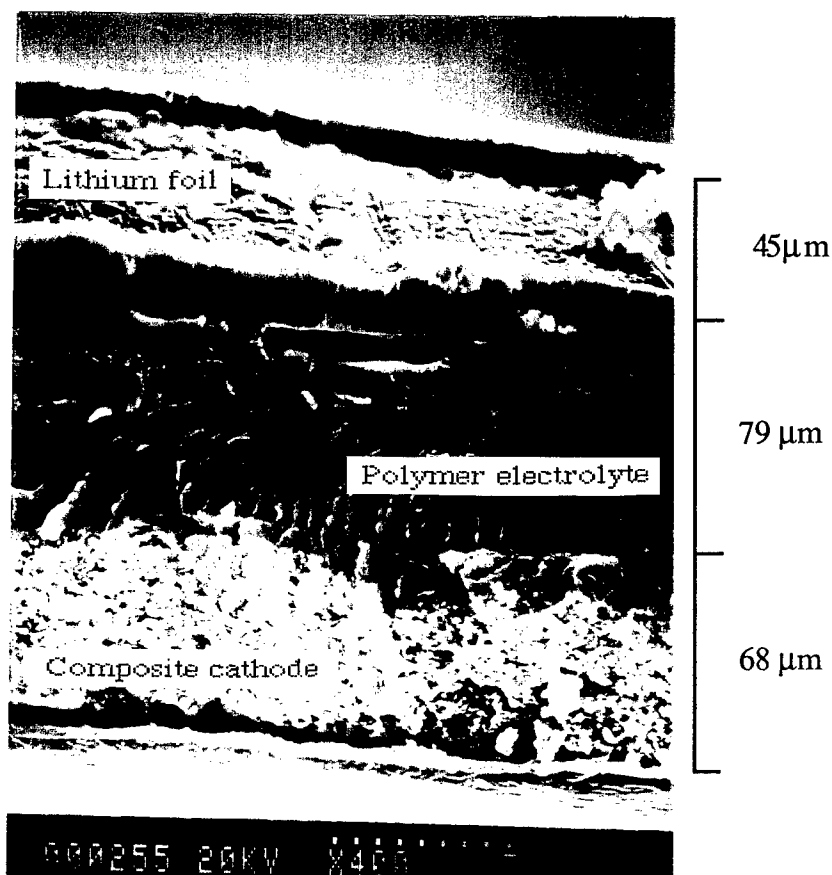
**Figure 22** A.c. impedance data after 8 cycles for Mark I LPB cell P106 cycling at 40% depth of discharge with a mixed mode charge.



**Figure 23** A.c. impedance data after 28 cycles for Mark I LPB cell P106 cycling at 40% depth of discharge with a mixed mode charge.



**Figure 24** A.c. impedance data for Mark I LPB cell P106 cycling at 40% depth of discharge with a mixed mode charge.



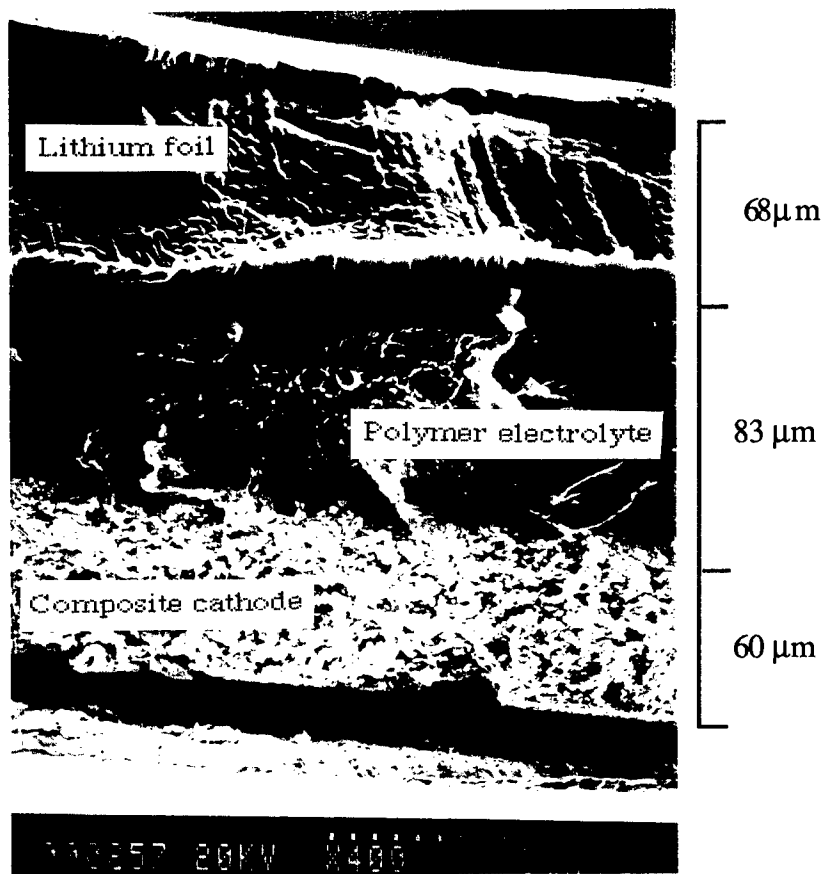
**Sample:** Standard HT cell (40 cm<sup>2</sup>) P075 D<sup>72</sup> C<sup>71</sup>

**Print no:** 000255 **Magnification:** X400

**Comments:** Fractured edge of complete cell

**Figure 25** *Scanning electron micrograph of the cross-section of Mark I LPB cell P075 after 72 cycles at 40% depth of discharge with a mixed mode charge.*



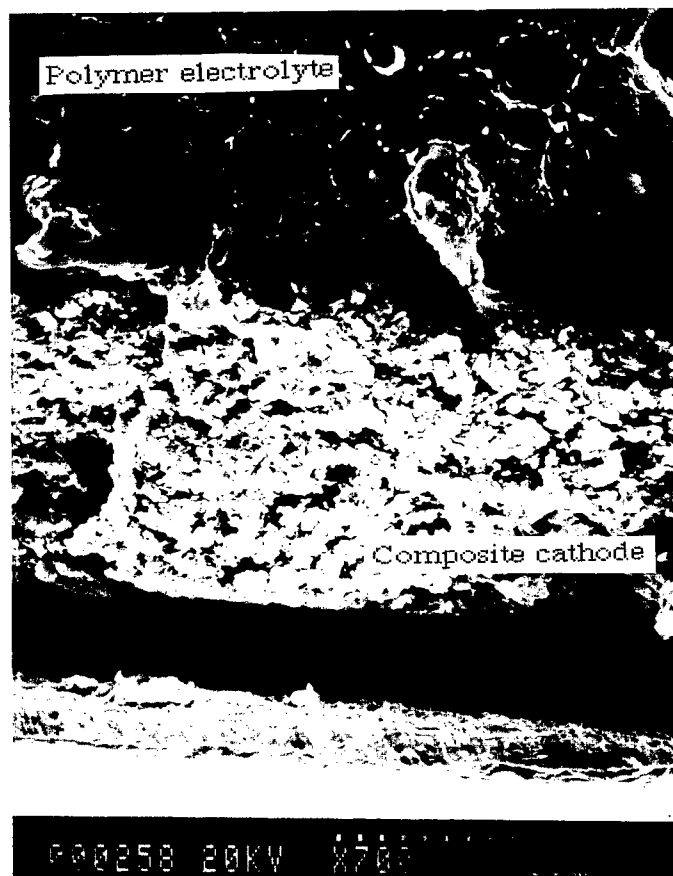


**Sample:** Standard HT cell (40 cm<sup>2</sup>) P075 D<sup>72</sup> C<sup>71</sup>

**Print no:** 000257 **Magnification:** X400

**Comments:** Fractured edge of complete cell

**Figure 26** Scanning electron micrograph of the cross-section of Mark I LPB cell P075 after 72 cycles at 40% depth of discharge with a mixed mode charge.

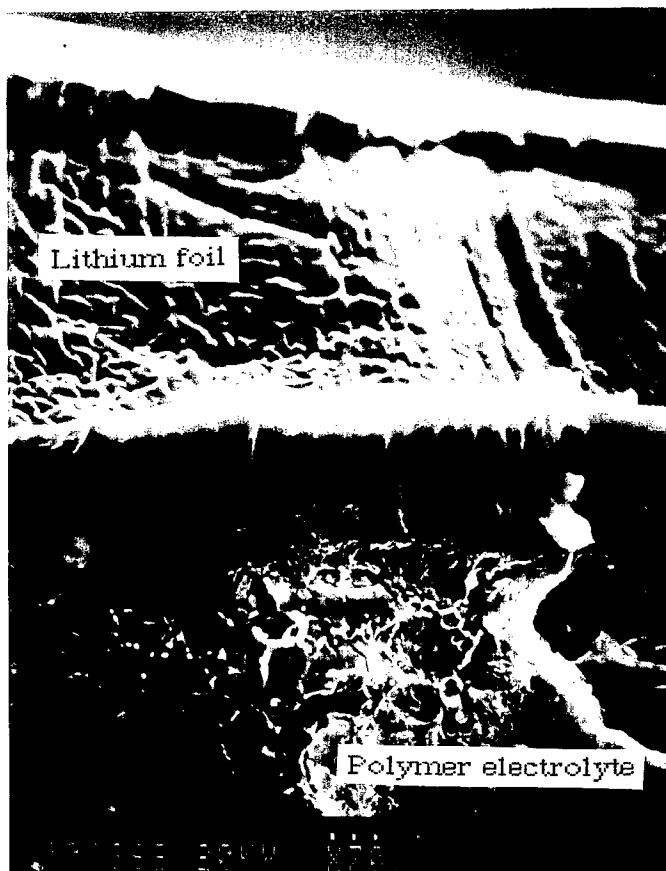


**Sample:** Standard HT cell (40 cm<sup>2</sup>) P075 D<sup>72</sup> C<sup>71</sup>

**Print no:** 000258      **Magnification:** X700

**Comments:** Fractured edge of complete cell

**Figure 27** *Scanning electron micrograph of the cross-section of cycled Mark I LPB cell P075 showing the polymer electrolyte/composite cathode interface in greater detail.*

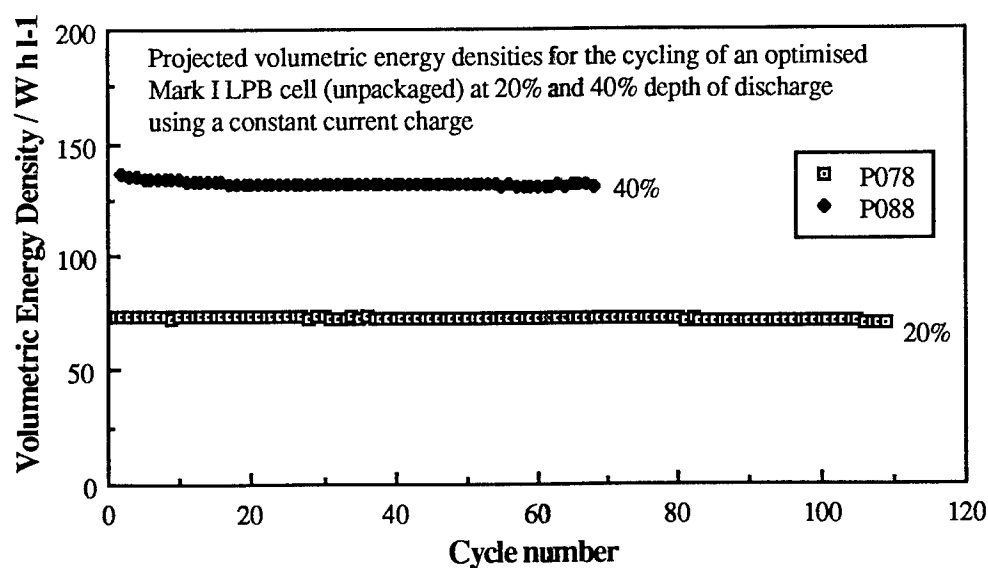
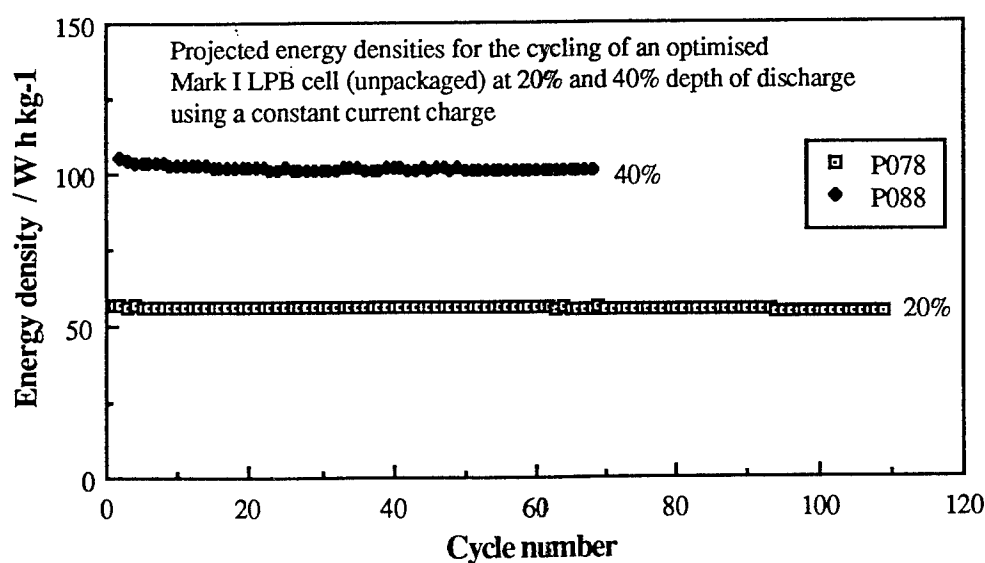


**Sample:** Standard HT cell (40 cm<sup>2</sup>) P075 D<sup>72</sup> C<sup>71</sup>

**Print no:** 000262 **Magnification:** X700

**Comments:** Fractured edge of complete cell

**Figure 28** *Scanning electron micrograph of the cross-section of cycled Mark I LPB cell P075 showing the polymer electrolyte/lithium interface in greater detail.*



**Figure 29** Projected energy densities for the cycling of an optimised Mark I LPB cell (unpackaged) at 20% and 40% depth of discharge using a constant current charge.

NB values assume an LPB cell with 50 $\mu$ m lithium foil, 85  $\mu$ m PEO<sub>12</sub>:LiClO<sub>4</sub> electrolyte and a 10 $\mu$ m aluminium current collector.

### **3. List of Publications arising from the Contract Work**

AEA Technology, Harwell Laboratory has published no materials resulting from the contract work.

AEA Technology, Harwell Laboratory has no current plans to publish any of the material resulting from the contract work.

### **4. Professional Personnel**

The following is a list of professional personnel who have contributed to the Contract Work. Dr Robin John Neat, Dr William James Macklin, Mr Raymond John Powell and Mrs Alison Jane Walker. None of these personnel were awarded an advanced degree during the duration of the project.

### **5. Interactions**

No interactions between Harwell staff and any organisation, other than the Program Manager and associated staff, has taken place on the subject of the contract work during the duration of the contract.

### **6. Inventions and Patents**

The contract work has not given rise to any inventions and AEA Technology, Harwell Laboratory has not filed or authorised others to file any patents arising from the contract work.

### **7. Additional Information**